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THE RECOVERY OF URANIUM FROM INDUSTRIAL PHOSPHORIC ACIDS BY SOLVENT EXTRACTION.
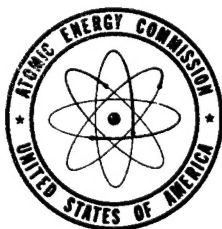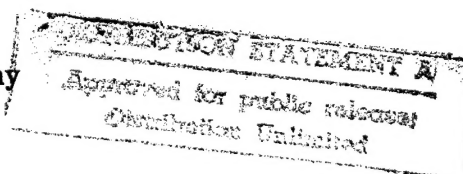
Part I. Summary Status Report.

Part II. Index of Monthly Progress Reports.

By
D. A. Ellis

July 14, 1952

Western Division
Dow Chemical Company
Pittsburg, California

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SUMMARY STATUS REPORT

THE RECOVERY OF URANIUM
from
INDUSTRIAL PHOSPHORIC ACIDS
by
SOLVENT EXTRACTION

Part I.   Summary Status Report
Part II. Index of Monthly Progress Reports

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Contract No. AT-30-1-GEN-236

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THE DOW CHEMICAL COMPANY
Western Division
Pittsburg, California

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I. ABSTRACT

SUMMARY STATUS REPORT

THE RECOVERY OF URANIUM
from
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SOLVENT EXTRACTION

JULY 14, 1952

THE DOW CHEMICAL COMPANY
Western Division
Pittsburg, California

A process for the recovery of uranium from industrial phosphoric acids by liquid-liquid extraction with alkyl ortho- and pyro-phosphoric acids is described. Studies of the chemistry and mechanics of the extraction process and various methods for recovery of uranium from the organic extract are reported.

II. <u>INTRODUCTION AND SUMMARY</u>

This report is a summary of the work done at this laboratory from March, 1951, through June, 1952, on the recovery of uranium from industrial phosphoric acid by solvent extraction. This work has been reported in the monthly progress reports for this period. An index of the topics discussed in the monthly progress reports is also included to facilitate reference to the original data.

The solvent extraction process developed at this laboratory consists of the following steps:

        a. Contacting the acid with a solution of alkyl pyro-phosphoric acid in a suitable diluent.

        b. Separation of the phases.

        c. Removal of the extracted uranium from the organic phase by precipitation with HF or other reagents, or by re-extraction into other solutions.

Most of the work has been done with acid from Company A. Studies have been made of the effects of oxidation potential of the acid, of treatment with silicious materials, of temperature of the acid, and of phosphate concentration of the acid.

A number of alkyl phosphoric and pyro-phosphoric acids have been tested. The methods of manufacture, the effects of structure on the extraction, and the use of various diluents have been investigated.

A multistage countercurrent mixer-settler has been constructed and operated under various conditions. This has made possible the production of considerable quantities of uranium-containing extract.

An extensive study was made of the precipitation of uranium from organic extracts with HF. A few precipitations were made with ammonia. Extraction of uranium from the organic solutions with concentrated phosphoric acid and with hydrochloric acid solutions was also studied.

An investigation was made of the breakdown of the extractants under various conditions, and of methods of rejuvenation that would enable the extractants to be recycled.

A small amount of work has been done with commercial phosphoric acids from Companies C, E, H and K.

Various modifications in analytical procedures were developed, both for uranium analysis and for the determination of the composition of the extractants.

This report is a presentation of the significant findings of this work and of the conclusions and recommendations that have been drawn.

III. Extraction of Uranium from Company A
      Phosphoric Acid

      A. Measurement of Magnitude of Extraction
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Extraction of Uranium from
Company A Phosphoric Acid

A. Measurement of Magnitude of Extraction

Single-stage Extraction

Most of the data in this study have been obtained by
single-stage extractions. The procedure consists of measuring
a volume of acid and a volume of extractant into a separatory
funnel, shaking for one to two minutes, separating the phases,
and analyzing each phase for uranium. For conservation of mass,

$$C_H = C_O V_O / V_A + C_A$$

where C_H is the uranium concentration of the head acid.
C_O is the uranium concentration of the organic phase.
C_A is the uranium concentration of the aqueous phase.
V_O is the volume of the organic phase.
V_A is the volume of the aqueous phase.

The magnitude of the extraction can be indicated either
by the per cent of uranium extracted from the acid or by the dis-
tribution coefficient.

Per cent Extraction

The per cent extracted is calculated from the expression
$100(1-\frac{C_A}{C_H})$. It is a function of the ratio of organic to aqueous
phase. Thus extractions under different conditions can be compared
by plotting per cent extracted vs. this volume ratio and comparing
the curves. A per cent extracted value is, of course, meaningless
for purposes of comparison unless the volume ratio is also given.

Distribution Coefficient

The distribution coefficient is the ratio of the uranium
concentration in the organic to that in the aqueous phase (C_O/C_A).
In the case where the isotherm (the plot of C_O vs. C_A) is linear,
the distribution coefficient is not a function of the ratio of the
volumes of organic to aqueous phase. Hence, the distribution co-
efficient alone may be used as a measure of the magnitude of ex-
traction without specifying the volume ratio. It has been found
that in the range studied, the isotherms are linear for extraction
of uranium from phosphoric acids when ortho-phosphates or concen-
trated solutions of pyro-phosphates are used for extractants. The

symbol K_D is used for the distribution coefficient.

$$K_D = \frac{C_O}{C_A}$$

K_D is a function of the concentration of the extractant in the organic solution. A plot of K_D vs. volume fraction of extractant in the organic solution shows this relationship. In all cases that have been investigated during this study, this relationship has been found to be linear. The slope of this plot (K_D/volume fraction extractant in organic solution) is a value dependent neither on the phase ratio nor the concentration of extractant. This value has been designated K^x. It is the coefficient for the distribution of uranium into undiluted extractant.

The function which gives the best comparison between extractions, where phase ratio and extractant concentration are not constant, is K^x. However, the function of interest in engineering and plant design is K_D.

Precise Determination of the Distribution Coefficient

In many of these studies, distribution coefficients have been determined from single extraction experiments. Since there is a large variance associated with the uranium analyses, the distribution coefficients obtained from a single experiment are not of the desired precision. The coefficients can be measured more accurately by determining the isotherm from a number of experiments at different phase ratios and measuring the slope. The isotherm is obtained by plotting either C_O vs. C_A or C_O/volume fraction extractant in organic vs. C_A. In the first case the slope is K_D. In the second case the slope is K^x. A typical linear isotherm obtained with octyl phosphoric acid is shown in Figure 1 A.

In the case of dilute solutions of pyro-phosphates, the isotherms are not linear, but are concave toward the C_A axis. It is believed that this is the result of the organic phase becoming saturated with uranium. This situation is analogous to the problem of gas adsorption in a single layer which has been treated by Langmuir. Following the same reasoning, an equation can be derived for this case:

Figure 1. Typical Equilibrium Isotherms for the Distribution of Uranium between Company A Phosphoric Acid (30% P₂O₅) and Extractants

A. 20% O.P.A. in kerosene; Acid at -0.142 v., 25° C.
B. 2% O.P.P.A. in kerosene; Acid at -0.145 v., 25° C.
C. Plot of K^* vs. C_O^A; Same data as B.

$$K^{\#} = K^{\#}_{max} - K^{\#}_{max}C^{\#}_{O}/C^{\#}_{max}$$
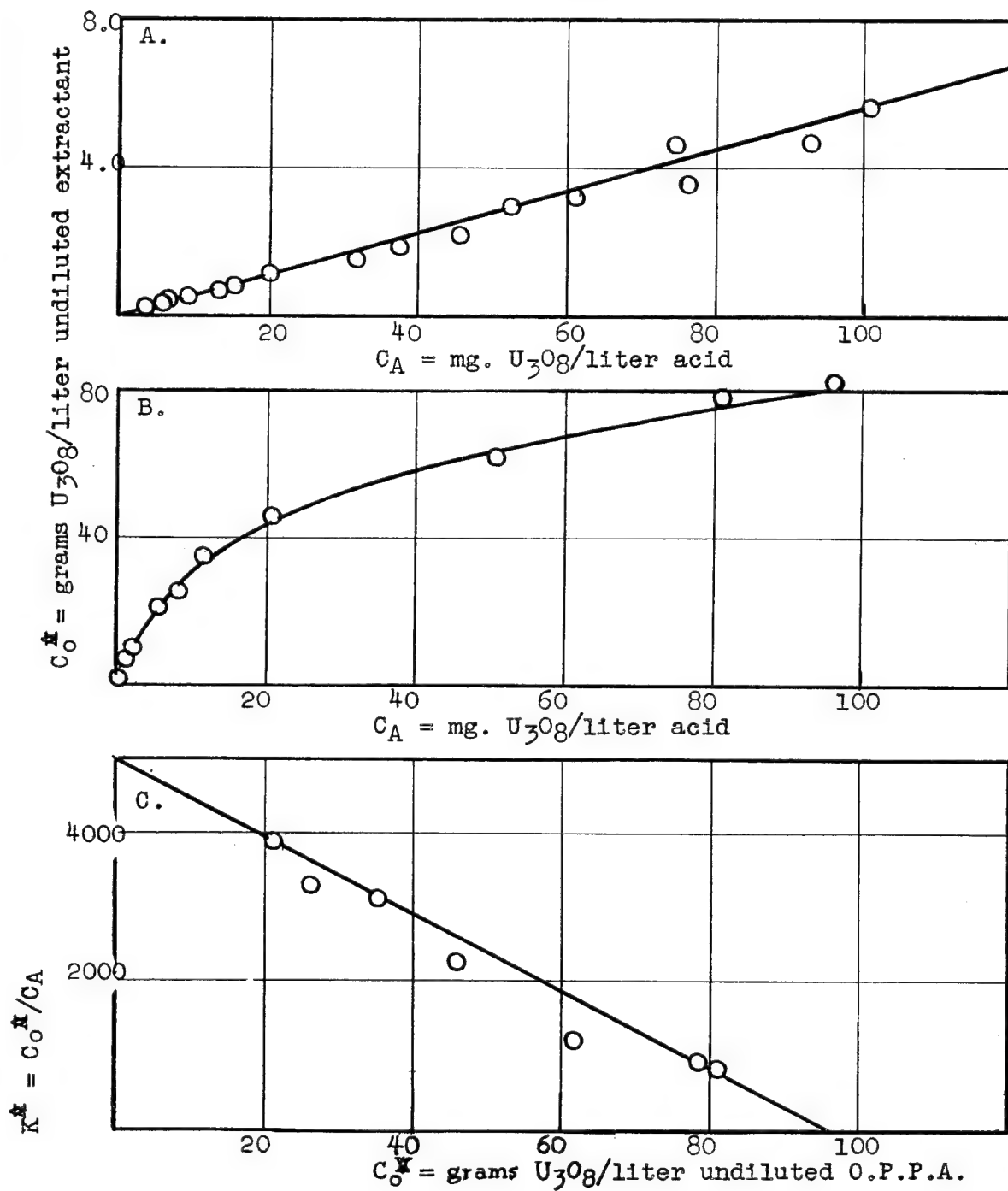
where $K^{\#}$ is the coefficient for the distribution into undiluted extractant

$K^{\#}_{max}$ is the maximum value of $K^{\#}$

$C^{\#}_{O}$ is the concentration of uranium in the pure extractant

$$C^{\#}_{O} = C_{O}/\text{volume fraction of extraction in organic phase}$$

$C^{\#}_{max}$ is the saturation value of $C^{\#}_{O}$

Thus $K^{\#}$ vs. $C^{\#}_{O}$ should give a linear plot. The intercept on the $K^{\#}$ axis is $K^{\#}_{max}$. The intercept on the $C^{\#}_{O}$ axis is $C^{\#}_{max}$. A typical curved isotherm obtained with octyl pyro-phosphoric acid is shown in Figure 1 B. A linear plot of $K^{\#}$ vs. $C^{\#}_{O}$ for the same data is shown in Figure 1 C.

Calculation of Multistage Behavior from Distribution Coefficients

An equation relating the per cent recovery in a multistage plant to the distribution coefficient, for the case of a linear isotherm, is given in Treybal[1]. On translating the symbols into those used in this paper the following equation is obtained for the per cent recovery in n stages when the feed extractant contains no uranium.

$$\frac{\% \text{ extracted}}{100} = \frac{(K_D V_O/V_A)^{A+1} - (K_D V_O/V_A)}{(K_D V_O/V_A)^{A+1} - 1}$$

V_O/V_A is the ratio of the flow rates of organic to aqueous phase.

Figure 2 presents this equation in graphical form. From this graph, the theoretical recovery can be obtained for a given number of stages, distribution coefficient, and phase ratio.

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[1] Treybal, R. E., *Liquid Extraction*, (1st ed.; McGraw-Hill Book Company, Inc., New York, 1951), p. 174.

Figure 2. <u>Per Cent Extracted vs. $K_D V_O/V_A$ for n Stages.</u>
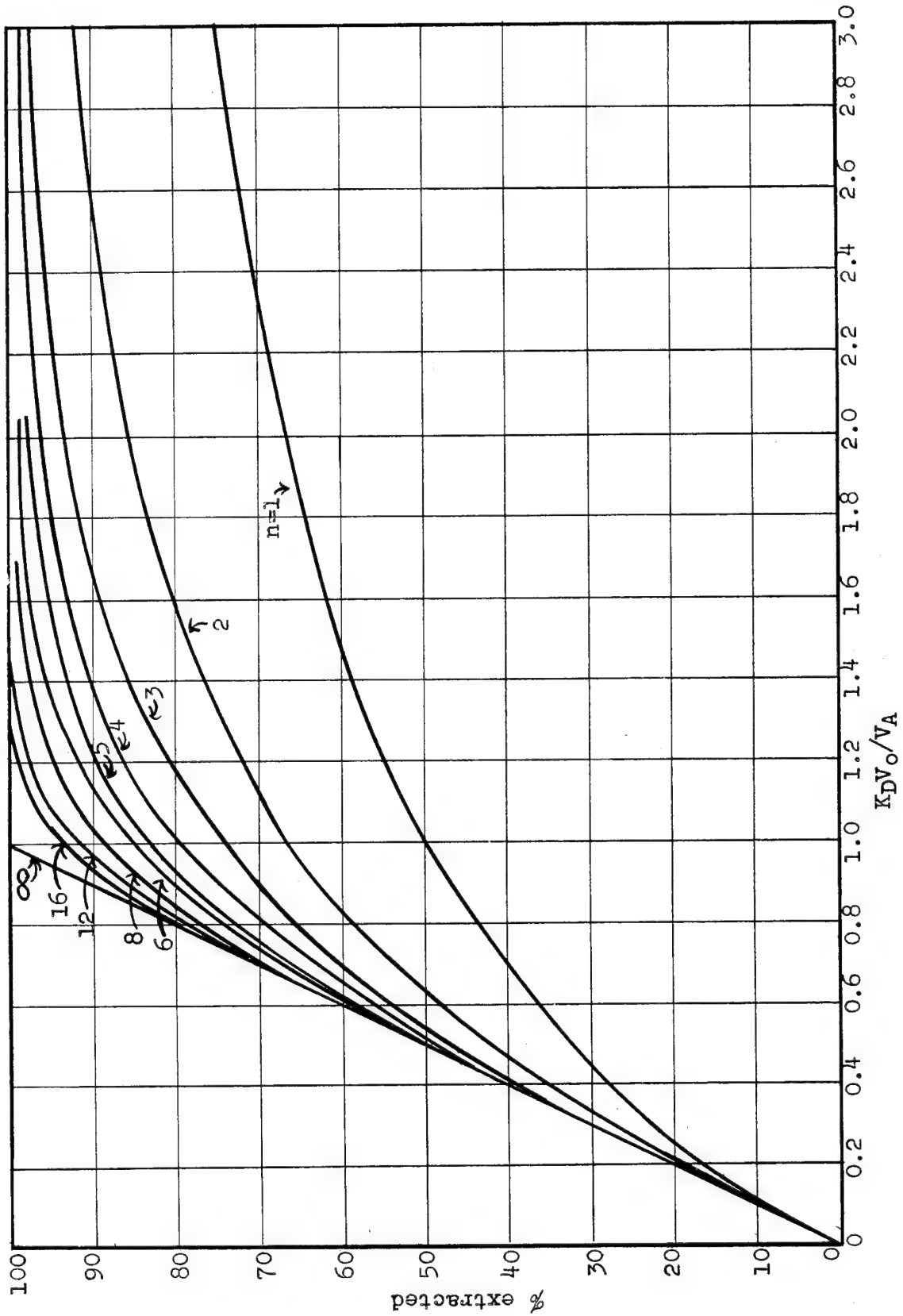
B. Study of Variations in Acid by Single-stage Extraction

Analysis of the Acid

A number of samples of acid have been received from Company A. The analyses of these samples are shown in Table I. Lot 1 was a batch of acid received by tank car. This was left over from the ion-exchange studies and was used from March, 1951, to January, 1952. Lot 2 was received in six 55-gallon drums and was used from January, 1952, to June, 1952. The other batches were weekly samples received in waxed or polyethylene bottles.

A comparison of the analyses of Lots 1 and 2 with the analyses of the weekly samples indicates that the large lots do not differ greatly from the weekly samples. However, Lot 2 appears to be more reduced than Lot 1 and also to have a lower ratio of fluoride to silica.

Reduction of the Acid

There is an indication that the extractants used in these experiments tend to be more selective for highly charged ions. Thus reduction improves the extraction in two ways, by reducing UO_2^{+2} ion to U^{+4}, and by reducing Fe^3 to Fe^2. The latter reaction lowers the amount of iron extracted.

The relation between oxidation potential and ratio of ferrous to ferric ion has been determined to be

$$E = -0.200 + 0.06 \log_{10} (Fe^2)/(Fe^3)$$

where E is the oxidation potential in volts (Pt vs. S.C.E.). This equation gives the slope which would be predicted by the Nernst equation.

The potential of synthetic phosphoric acid solutions was also studied. The oxidation state of solutions containing 10, 20, and 30% P_2O_5 was varied by addition of different ratios of ferrous and ferric salts. A plot of e.m.f. vs. $\log_{10} Fe^2/Fe^3$ gave approximately the theoretical stope. E_o in this case was -0.210 volts. There seemed to be no effect of phosphate concentration.

Most of the reduction studies have been made using iron as the reductant. Company A desires that a minimum of iron be added to the acid. They would prefer the addition to be not more than 4 or 5 grams of iron per liter. The acid contains from 5 to 8 grams per liter initially. As this is present as ferric ion, the stoichiometric quantity of iron which must be added to reduce the iron in the solution is 2.5 to 4 grams per liter.

TABLE I

Analysis of Company A Phosphoric Acid

	Lot 1	Lot 2	10-25-51	11-2-51	11-6-51	11-14-51	11-20-51	12-6-51
U_3O_8 (mg./liter)	112	99.6	130.5	121.8	112.5	147.2	123.6	138.6
PO_4 (grams/liter)	525	549.0	545	490	613	554	545	602
SO_4 (grams/liter)	39.26	34.7	55.7	52.4	47.2	25.4	27.13	50.13
Fe^2 (grams/liter)	0.045 ⎫	5.6 ⎫	0.158	0.334	0.43	<0.118	0.021	0.17
Fe^3 (grams/liter)	6.30 ⎭	⎭	5.39	5.43	7.37	8.33	7.21	8.25
F^- (grams/liter)	20.3	18.45	24.1	21.5	19.5	19.6	16.1	18.5
Si^- (grams/liter)	4.11	7.6	6.75	2.64	2.19	2.03	3.24	3.45
Sp. Gr.	1.33	------	1.329	1.318	1.328	1.198	1.3281	1.3635
e.m.f. (volts vs. S.C.E.)	-0.420	-0.225	-0.345	-0.220	-0.270	-0.222	-0.300	-0.240

A number of experiments were performed at room temperature using powdered iron of very high purity. This type of iron is quite expensive and thus would not be used in a commercial plant. The reduction was accomplished by adding the iron to the acid in a 75-gallon tank and stirring. The rate of reduction was increased with increasing agitation as long as air was not mixed with the solution. The reduction was accompanied by mild evolution of hydrogen. This caused a froth which served as a blanket, keeping the solution from contact with air. A potential of +0.170 V (Pt vs. S.C.E.) was reached in about 50 minutes with solution of 3.5 grams of iron per liter. The addition of 4 grams of iron per liter resulted in a potential of +0.200 V. When the solution was stirred too vigorously, air was mixed in and the reduction was less complete.

Some experiments were performed with iron powder of 93% Fe obtained from the American Steel Abrasive Co. This type of iron costs about $0.065 per pound. The results at room temperature were similar to those with pure iron. A positive e.m.f. was obtained with solution of 4 grams per liter. However, it was necessary to add 6 grams of iron per liter in order to obtain solution of 4 grams. The rest of the iron is slowly soluble and does not seem to cause further reduction.

Tests were made with the 93% iron at 60 to 65° C. The iron dissolved more rapidly and more completely than at room temperature, but reduction was no faster. Thus with the unpure on powder, a low temperature and removal of undissolved iron is sirable for reduction unless addition of about 7 grams of iron per liter is permissible.

A sample of scrap iron was obtained in the form of "nail whiskers". This type of iron consists of trimmings from the manufacture of wire nails. It costs about $0.02 per pound. The particles varied in size, but most were -14+18 mesh.

A few preliminary tests were made in a stirred tank. In each case 6 grams was added per liter of acid. At room temperature the iron dissolved slowly, but almost no reduction was accomplished. At 60 - 65° C., the reduction was slow, but a positive e.m.f. was attained in 4 hours. By this time, 5 grams of iron had dissolved per liter.

In order to attain reduction in a reasonable length of time, a column of -14+18 mesh "nail whiskers" was set up. The column was a water-jacketed glass tube, one inch ID, packed to a height of 33 inches. The void fraction was about 0.5. The acid was passed upflow through the column. Runs were made at various flow rates and various temperatures. It was found that

reduction to a positive e.m.f. was attained only at high temperatures, but at these temperatures the amount of iron dissolved in the acid was excessive. When the feed rate at room temperature was decreased below 5 ml./(min.)(cm.^{2}), the reduction was not increased, but there was greater consumption of iron and evolution of hydrogen.

The height of the iron in the reduction column was increased to 65 inches. With this column it was found that high reduction could be attained at flow rates from 25 to 100 ml./(min.)(cm.^{2}) by proper adjustment of temperature.

Runs were also made with the 1-inch by 65-inch column packed with 8-mesh "nail whiskers" and packed with "nail whiskers" as received without screening. When the 8-mesh iron was used, the 65-inch column was not long enough to provide enough surface for good reduction. However, when an 88-inch column was used, good reduction was observed. When the iron was used without screening, the reduction in the 65-inch column was approximately the same as when only -14+18 mesh particles were used.

The 1-inch by 65 inch column with unscreened nail whiskers was used in conjunction with the multistage mixer-settler. It provided adequate reduction for good recovery of uranium from the acid, with iron consumption of about 4 grams per liter.

The iron in the column was found to give better reduction with lower consumption of iron when it was first washed with 2N HCl.

Several difficulties were encountered in operating the 1-inch columns. At the higher temperatures and lower flow rates, hydrogen evolution during reduction caused small particles of iron to rise in the column and to be swept out with the acid. When the "nail whiskers" were used as they were received, small chips of wood and dirt which were present felted with the iron particles to form plugs. Both these difficulties would probably be eliminated by the use of a larger diameter column.

A number of other reductants were tried. Aluminum and zinc were effective. Aluminum may compete cost-wise with some types of iron, but zinc would be much more expensive. Addition of 2 grams of aluminum per liter to a stirred vessel of acid gave a positive e.m.f. in 45 minutes. Copper and lead did not reduce the acid, nor did sodium hydrosulfite or formaldehyde. Treatment with H_2S and SO_2 gave some indication of reduction, but the extraction coefficients obtained with acid so treated were not significantly different from those obtained with untreated acid.

A cell was constructed to reduce the acid electrolytically. Overall efficiencies of up to 60% were obtained. However, it was necessary to use a very low current density to realize reasonable efficiencies. Hence, a commercial plant to reduce the acid electrolytically would be too large to be economically feasible.

Effect of Oxidation Potential of the Acid

The extraction of uranium is greatly improved if the acid is first reduced. This has been found with amyl, butyl, and octyl phosphoric acids and with octyl pyro-phosphoric acid. The cases of octyl phosphoric acid (O.P.A.) and octyl pyro-phosphoric acid (O.P.P.A.) were studied in quite some detail. Isotherms were determined at various potentials with various concentrations of O. P.A. and O.P.P.A. in kerosene. Figure 3 shows plots of log K^* vs. e.m.f. It is evident that reduction from -0.300 to 0.0 volts increases the distribution coefficient of O.P.A. solution over ten times and that of O.P.P.A. solutions over twenty times.

Effect of Addition of Siliceous Materials to the Acid

Extraction of uranium from Lot 1 Company A acid was enhanced when the acid was stored in glass vessels or treated with siliceous materials. This was quite a large effect. The distribution coefficient was between two and three times higher after treatment. The comparison between extraction coefficients obtained with acid treated with siliceous materials and acid not so treated is shown in Figure 3. As the reaction between the acid and glass was slow, glass vessels could be used for the extractions in this study without appreciably affecting the results. About eight days were required for equilibrium between the acid and glass when the acid was allowed to stand in a glass vessel. The rate of reaction was increased by stirring, but three to four says were still required. Addition of glass wool, sand, or silica gel increased the rate further, but more than two days were still required for equilibrium. Diatomaceous earth, however, reacted much faster. When the acid was stirred for two hours with diatomaceous earth, the distribution coefficients were as high as those obtained with acid which had been stored in glass for eight days.

The effect of siliceous materials is probably due to the presence of fluoride in the acid in excess of the amount necessary to complex all of the silica present. To test this, fluoride was added to Company A acid which had been treated with siliceous materials. It was found that the decrease in distribution coefficient of O.P.A. solutions due to adding 2 grams of fluoride per liter of acid was equivalent to the increase obtained by treating with siliceous materials.

Figure 3. K_{max}^{*} vs. Oxidation Potential for the Distribution of Uranium between Company A Phosphoric Acid and Extractants at 25° C.

☐ O.P.A. solns. in kerosene;Acid not treated with siliceous mat'l.
△ O.P.A. solns. " " ;Acid treated with siliceous mat'l.
◯ O.P.P.A. " " " .Acid not treated with siliceous mat'l.
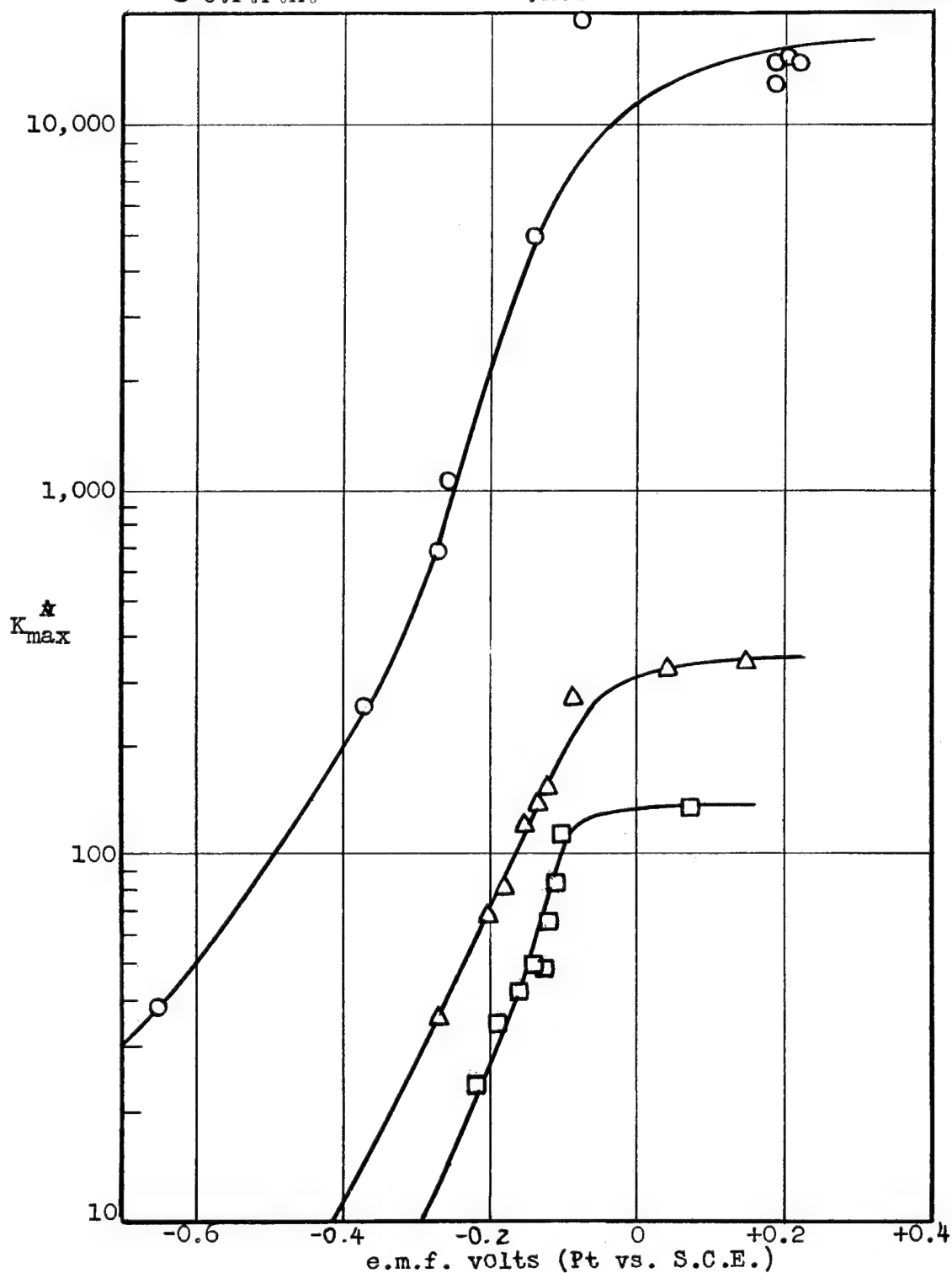
The effect of adding fluoride to a synthetic phosphoric acid (30% P_2O_5) containing uranous ion was also studied. It was found that the extraction coefficient with O.P.A. solutions continued to decrease as the fluoride concentration was increased. The addition of 2 grams HF per liter of acid reduced K_D to 50% of the value for acid without fluoride. The addition of 10.9 g. HF per liter of acid reduced K_D to 10% of the original value. When O.P.P.A. was used as the extractant, the decrease in coefficient with added fluoride was not as great. Thus 10.9 g. HF per liter of acid reduced K_D only 30%.

The effect of addition of silico-fluoride to the synthetic acid was also studied. H_2SiF_6 and Na_2SiF_6 were added to the acid and extractions were made with O.P.P.A.-kerosene solutions. There was no measurable effect on the distribution coefficient.

Extraction from Lot 2 Company A acid was not affected by treatment with diatomaceous earth. In this case the extraction experiments were made with octyl pyro-phosphoric acid. Lot 2 acid contained a lower mole ratio of fluoride to silica than did Lot 1. Thus, the ratio of fluoride to silica in Lot 1 was 7.3, while in Lot 2 the ratio was only 3.6. In fluosilicate it is 6.0. It appears then, that Lot 1 had insufficient silica to combine with all of the fluoride and hence the addition of siliceous material improved the extraction by tying up the excess fluoride. Lot 2, however, contained more than enough silica to complex all of the fluoride, so the addition of siliceous material had no effect. As all the work with alkyl pyro-phosphoric acids has been done with Lot 2 acid, the effect of addition of silica to Company A acid has not yet been determined with pyro-phosphates.

Effect of Phosphate Concentration of the Acid

The concentration of phosphate in Company A acid was varied by dilution with water, concentration with C.P. 85% H_3PO_4, and by evaporation. Isotherms were measured for the extraction of uranium from both unreduced and reduced acid with O.P.A.-kerosene solutions. Log log plots of K^* vs. phosphate concentration indicated that K^* varied approximately as the inverse fourth power of phosphate concentration. Extraction coefficients were similarly obtained from synthetic phosphoric acid solutions to which uranium had been added. It was found that in this case, the relation between K^* and phosphate concentration was inversely linear.

Extraction coefficients of solutions of varying phosphate content were also measured with O.P.P.A.-kerosene solutions. For the region investigated (21-51% P_2O_5) the modified Company A solutions showed no appreciable effect of phosphate concentration on the value of K^*. Synthetic phosphoric acid solutions, however, showed an inverse linear relationship between K^* and phosphate concentration in the region 10 - 30% P_2O_5.

Effect of Ammoniation of the Acid

A study of the extraction of uranium from partially ammoniated Company A phosphoric acid indicated that ammoniation decreases the extraction coefficient with either O.P.A. or O.P.P.A. solutions. The decrease is greater in the case of O.P.P.A. solutions.

Effect of Temperature of the Acid

Higher temperatures have been found to lower the distribution coefficient. A number of experiments with a batch of O.P.A. that had been on hand for several months indicated that with reduced acid K^a decreased about 25% as the temperature of the acid was raised from 22 to 55° C., but with unreduced acid K^a decreased about 40% between 22 and 55° C. Experiments with a fresher lot of O.P.A. indicated that the decrease was about four times as great in both cases for the same change in temperature. It may be that in the case of the fresh O.P.A., part of the extractant is hydrolized at higher temperatures to compounds which are more stable but are poorer extractants.

Extractions have also been made with O.P.P.A. solutions and acid at elevated temperatures. The values of K^a_{max} for both unreduced and reduced acids at 50° C. were only about 30% at the values obtained at 25° C. One minute shaking time was used in these experiments. There was a further large decrease in K^a when the temperature of the acid was raised to 70° C. The magnitude of the temperature effect is a function of the time of contact of the acid and extractant at the elevated temperatures. The effect seems to be due, at least in part, to a degredation of the extractant. Thus when acid and O.P.P.A.-kerosene solution were mixed for two hours at 70° C. and then cooled, the value of K^a was only four. With fresh O.P.P.A. and the same acid mixed at room temperature, K^a was 1200.

Extraction of Other Metals from the Acid

Various metals which are found in commercial phosphoric acids were added to a synthetic phosphoric acid solution (30% P_2O_5) and extractions were made with O.P.A.-kerosene solutions. The distribution coefficients of uranium (IV) and thorium (IV) were very high. The coefficient for ferric and cerous ions were appreciable but all other ions tested showed quite low extraction.

Comparison of Weekly Samples of Company A Acid

Weekly samples of acid were obtained from Company A for six weeks. The analyses of these acids are give in Table I. Isotherms were determined for the extraction of uranium from each

sample at two different oxidation potentials. It was found that the distribution coefficients were as high, and in some cases higher than those obtained with Lot 1 acid. It was concluded that the extraction data obtained from Lot 1 was typical of the data that would be obtained in an actual plant at Company A.

Composition of Acid after Extraction

Several analyses have been made of the acid raffinate after extraction. Except for the low uranium content, the analyses showed little difference from the head acid. The iron concentration was higher when iron had been used as a reductant. The titanium vanadium and aluminum concentrations were slightly lower than in the head acid.

Conclusions

The following conclusions can be drawn from the study of acid variables.

If it is required that the acid be reduced, scrap iron would be the cheapest reductant of those tested.

Reduction with scrap iron is done most efficiently in a column.

About 4 grams of iron per liter of acid are required for reduction to a positive potential. This amount will, of course, vary with the original ferric concentration in the acid. The stoichiometric amount of iron necessary for complete reduction of iron is equal to half of the amount of ferric ion contained in the acid originally.

The extraction coefficients with both alkyl ortho-phosphoric acids and alkyl pyro-phosphoric acids are greatly improved if the acid is first reduced.

Treatment of the acid with siliceous materials increases the extraction when fluoride is present in the acid in excess of the amount necessary to complex all of the silica.

The distribution coefficient with O.P.A. solutions varies approximately as the fourth power of the phosphate concentration of the acid. With O.P.P.A. solutions, the distribution coefficient is not greatly affected by phosphate concentration.

The extraction with both O.P.A. and O.P.P.A. solutions is adversely affected by increase in temperature. With O.P.P.A. solutions there is considerable deterioration of the extractant when treated with acid at elevated temperatures.

C. Study of the Extractant

Preparation of Extractants

A number of alkyl ortho-phosphoric and pyro-phosphoric acids were obtained from Eastman Kodak Company, Monsanto Chemical Company, and Victor Chemical Company. Most of the studies with ortho-phosphoric acids were made with these commercial samples. Most of the studies with pyro-phosphoric acids, however, were made with preparations made at this laboratory.

The organic phosphoric acids are prepared by mixing P_2O_5 and alcohol. The ratio of alcohol to P_2O_5 determines the nature of the product. Thus, a 3:1 mole ratio should give about equal mole quantities of mono- and di-alkyl ortho-phosphoric acid according to the equations

$$3ROH + P_2O_5 \longrightarrow RH_2PO_4 + R_2HPO_4$$
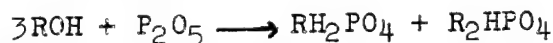
This is the approximate composition of the commercial alkyl ortho-phosphoric acids. By varying the mole ratio from 4:1 to 2:1 the product can be made to vary from 70 to 35% dialkyl.

If a 2:1 mole ratio is used the dialkyl pyro-phosphoric acid is formed:

$$2ROH + P_2O_5 \longrightarrow R_2H_2P_2O_7$$
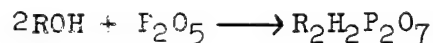
Actually, these reactions are more complex than this so that in the first reaction above some pyro-phosphoric acids are formed and in the second reaction some ortho- and perhaps some poly- and meta-phosphoric acids are formed.

Attempts have been made to prepare polyphosphoric acids by using a smaller mole ratio of alcohol to P_2O_5 than 2:1. There is a tendency in these reactions to form heavy viscous phases which are difficult to dissolve in kerosene or benzene. It is possible that polymeta-phosphates may be forming as well as poly-orthophosphates.

The initial method used in these preparations was to add the solid P_2O_5 to the alcohol slowly with stirring. This method is superior to the addition of alcohol to P_2O_5 as the latter reaction is rather violent. However, the direct addition of P_2O_5 has several disadvantages: the mixture heats up to about 120° C.; it is fairly viscous so that stirring is difficult, the P_2O_5 tends to coagulate into a sticky ball, and even if the clumping is overcome by proper agitation, the dissolution of P_2O_5 is slow.

Most of these difficulties are eliminated if the P_2O_5 is first slurried with a diluent and the alcohol is added to the slurry. The maximum temperature of the reaction is then determined by the heat capacity of the system or the boiling point of the solvent. This method has the further advantage of producing products which extract uranium better.

While these methods do not produce pure ortho- or pyro-phosphoric acids, in this report the product of the reaction of a a 3:1 mole ratio of alcohol to P_2O_5 are referred to as "alkyl ortho-phosphoric acids" or simply "alkyl phosphoric acids" and the product of the reaction of a 2:1 mole ratio are referred to as "alkyl pyro-phosphoric acids."

Extractions of uranium from Company A acid with octyl pyro-phosphoric acids prepared in various ways indicate that preparations made using the P_2O_5 slurries gave distribution coefficients about twice as high as those prepared by direct addition of P_2O_5 to the alcohol. A number of diluents for the preparation of the slurry were tried. It was found that kerosene, benzene, or diethyl ether could be used as diluents. Coefficients, obtained with preparations made with each of these diluents, were approximately equal. Kerosene is belived to be the most practical because of its low cost and also since kerosene is used to dilute the extractant before use. The maximum distribution coefficients were obtained with preparations made from slurries containing 0.1 to 0.2 g. P_2O_5 per ml. of kerosene.

A number of preparations were made in which the kerosene and the alcohol were dried before use. Extractions of Company A acid made with these preparations did not give significantly different coefficients than those with preparations made without drying.

Preparations were made with varying ratios of alcohol to P_2O_5. The highest extraction coefficients were obtained with a mole ratio of alcohol to P_2O_5 of 2:1.0. Preparations made with greater amounts of P_2O_5 tended to form a viscous second phase.

Preparations were made at various temperatures from 0 to 150° C. Extraction experiments indicated that the coefficient decreased with increase in temperature, but the effect was slight.

Inferior Extractants

Various extractants, some obtained commercially and some prepared in the laboratory were tested by means of single-stage extraction with Company A phosphoric acid. The following compounds

extracted no uranium within the error of the experiment:

       butyl acetate
       butyl ether
       butyl oxalate
       Freon 113

The following compounds extracted uranium only slightly:

       tri-butyl phosphate
       tri-cresyl phosphate
       butyl citrate
       butyl bisulfide
       butyl isothiocyanate
       octyl chloride
       butyl borate

Benzene phosphonic acid and benzene phosphinic acid were prepared but proved to be fairly soluble in phosphoric acid.

Alkyl Ortho-phosphoric Acids

Extraction of Uranium

Solutions of alkyl ortho-phosphoric acids and alkyl pyro-phosphoric acids in organic solvents extracted uranium from Company A phosphoric acid with quite high distribution coefficients. A comparison of butyl ortho-phosphates and phosphites showed that in general phosphates extracted uranium better than phosphites. In both cases the mixtures of mono- and di- compounds extracted better than the tri- compounds. It was concluded that in general the -OH and =O groups contribute to the extraction and the compound with the greatest number of these groups extracts uranium the best.

Extractions with known mixtures of mono- and di-butyl ortho-phosphoric acid showed that there is a close dependence of the distribution coefficient on the mole ratio of di- to mono-. A ratio of approximately 2 di- to 1 mono- gave the maximum coefficient. This conclusion was confirmed with octyl ortho-phosphoric acids.

Comparison between commercial n-butyl, n-amyl, and n-octyl ortho-phosphoric acids indicated that the highest extraction was obtained with n-amyl on the basis of weight of extractant. Extractions with commercial normal, iso-, and secondary butyl ortho-phosphoric acids showed increased extraction as the branch of the chain was moved closer to the phosphate group. Octyl ortho-phosphoric acids showed the same effect.

Octyl was chosen as the best of the easily available ortho-phosphoric acids because of its low solubility in phosphoric acid compared with amyl.

Commercial samples of octyl ortho-phosphoric acid (O.P.A.) varied somewhat in extracting ability. Victor O.P.A. gave distribution coefficients about twice as high as Monsanto O.P.A. This may be because the Victor product was isooctyl, while the Monsanto product was normal octyl. The extraction efficiency of the first lot received from Victor seemed to decrease over a period of several months. The distribution coefficients obtained with the second lot received from Victor were about 1.3 times those obtained with the first lot when it was fresh.

It was found that the distribution coefficients obtained with O.P.A. could be increased by adding P_2O_5 to the extractant and stirring until the P_2O_5 was dissolved. This suggests that the difference between the two samples of Victor O.P.A. may have been due to a slow hydrolysis of some of the constituents of the first lot and that addition of P_2O_5 resulted in the reversal of this hydrolysis.

In these extractions, the extractant was dissolved in a solvent and the resulting solutions were shaken with the acid. A number of solvents have been tested by means of single-stage extractions of Company A phosphoric acid. With butyl phosphoric acid, kerosene and similar compounds could not be used, as the extractant was only partially soluble in them. Aromatic compounds gave higher distribution coefficients than aliphatic compounds. General Petroleum Aromatic Oil 1019 gave the highest extraction of any diluent tested. With octyl phosphoric acids, kerosene and similar compounds gave the best extractions. Thus, kerosene was used in most of the subsequent work as it is cheap and readily available. The kerosenes used here were commercial grades obtained from Associated Oil Company and Union Oil Company. They were obtained from western crudes.

Extractions were made with various concentrations of butyl, amyl and octyl phosphoric acids in organic solvents. In all cases it was found that the distribution coefficient was a linear function of the concentration of extractant in the organic phase at least for concentrations below 50%. This indicates that $K^{\bullet}$ (the distribution coefficient into pure extractant) is constant with varying concentration of extractant in the organic phase. There is some evidence that in synthetic C.P. phosphoric acid solutions containing uranium, the distribution coefficient is not a linear function of the concentration of extractant. In this case, $K^{\bullet}$ would lose much of its value in specifying the magnitude of the extraction.

Separation of Mono- and Di- Fractions

In order to determine optimum compositions of alkyl ortho-phosphoric acid mixtures, a study has been made of the methods of separation of the mono- and di- fractions.

Butyl phosphoric acid and amyl phosphoric acid in organic solutions can be separated into mono- and di- fractions by washing with water, as the mono- fraction is much more soluble in water. In this manner samples containing as high as 90% dibutyl phosphoric acid were prepared. However, the water solubility of octyl phosphoric acid is too low to permit separation of mono- and di-octyl phosphoric acids by this method.

O.P.A. solutions were separated successfully by precipitation of the mono- fraction with NaOH and acidifying the precipitate and supernatant liquor to reform the acids. The precipitations have been carred out both in alcoholic solution and in aqueous slurry. Fractions containing 85% mono- O.P.A. and fractions containing 80% di- have been obtained in this manner. An attempt was made to substitute lime for NaOH, but although an insoluble mono-salt was formed, jelly-like and taffy-like emulsions were also formed so that separation of the components was difficult.

The most successful method of separation of O.P.A. mixtures has been partition between two immiscible organic solvents. Several pairs of solvents have been tested. Of these, kerosene and ethylene glycol seem to give the best separation.

In this sytem, using equal volumes of kerosene and glycol, the distribution coefficient for mono-O.P.A. into kerosene is 0.055; for di-O.PA. it is 17. Hence, in a single stage, approximately 95% of the mono-O.P.A. goes into the glycol and approximately 95% of the di-O.P.A. goes into the kerosene. In a two-stage extraction, solutions containing over 99% mono- and di-, respectively, were prepared.

To separate the mono-O.P.A. from the glycol, the solutions were stirred with Dowex 1 anion resin in the hydroxide form. Titration of the glycol indicated that all acidity was removed from it by this means. The resin was washed with water and the mono-O.P.A. was eluted from the resin by stirring with a solution of HCl in methanol. The methanol solution was evaporated over night on a steam bath and a dark brown syrupy liquid separated. Titration of this liquid with NaOH indicated that it was the mono-O.P.A. fraction.

Substitution of Dowex 3 for Dowex 1 in this separation did not prove satisfactory, as the adsorption of the mono-O.P.A.

was slight. However, Permutit S and Duolite A-7 were found quite satisfactory.

Good separations have also been obtained with petroleum ether vs. ethylene glycol, kerosene vs. methanol water and petroleum ether vs. methanol water. This latter pair offers the advantage that both fractions can be recovered from the solution by evaporation of the solvent at room temperature.

O.P.A. mixtures have also been separated by passing through a column of silicic acid. Separation by ion exchange resins has not been successful, so far.

Solubility

The distribution loss of butyl and amyl phosphoric acids in water, especially of the mono- compounds, is high. Undiluted O.P.A. forms an emulsion when shaken with water. In one experiment, the emulsion was allowed to stand 36 hours, the O.P.A. which had settled out was removed, and the remainder of the emulsion was titrated with NaOH. The titration curve indicated a value of 0.10 g. di-O.P.A. and 6.4 g. mono-O.P.A. per liter of water. This approximates the upper limit for the loss of O.P.A. in water.

The distribution of O.P.A. between various solvents and water was studied by shaking O.P.A. solutions with water, separating the phases and titrating. It was found that from kerosene solutions of O.P.A., 3.9 g. of mono-O.P.A. was lost per liter of water. Petroleum ether and CCl_4 solutions of O.P.A. gave almost the same result.

The distribution of O.P.A. between solvents and C.P. 40% H_3PO_4 was studied by the same method. The solubility of O.P.A. in phosphoric acid was determined to be approximately 1 gram mono-O.P.A. per liter acid. The same result was obtained with a petroleum ether solution and with kerosene solutions of O.P.A. The volume ratio of organic to aqueous phase was varied, in the case of the kerosene solutions, from 0.05 to 0.4 and the per cent of O.P.A. in kerosene was varied from 10 to 30 but, in all cases, the loss was approximately 1 gram mono-O.P.A. per liter. There was no detectable loss of di-O.P.A.

The distribution of O.P.A. between kerosene and Company A phosphoric acid was measured. The O.P.A. solution was shaken with the acid and the dissolved O.P.A. was extracted from the acid phase with CCl_4. Titration of the CCl_4 with NaOH solution immediately after the initial break showed a solubility of 0.3 grams O.P.A. per liter of industrial acid. After standing over night

at room temperature the amount of O.P.A. in the acid was less than 0.004 g. per liter of acid, since most of the entrained O.P.A. had settled. Standing at 50° C. for 1 1/2 hours after shaking gave a distribution loss of less than 0.034 grams O.P.A. per liter of acid.

The solubility of C.P. phosphoric acid in O.P.A.-kerosene mixtures was also measured. Phosphoric acid of various concentrations was shaken with 10% solutions of O.P.A. in kerosene. The solubility was determined by estimating the concentration of free phosphoric acid in the organic solution by a colorimetric method using the vanado-phospho-molybdate complex. The amount of phosphoric acid dissolved was found to increase with phosphate concentration of the acid, but for 40% H_3PO_4 the solubility was less than 1/2 gram H_3PO_4 per liter of organic phase.

Hydrolysis

To determine the amount of hydrolysis of alkyl phosphoric acids, two samples were shaken with Company A phosphoric acid; one for a few minutes and the other for a number of hours. The phases were separated and the ratio of mono- to di- acid was determined by titration. The amount of hydrolysis was calculated from the difference in these two results. Butyl phosphoric acid indicated a maximum hydrolysis of 5 to 10% in 64 hours at room temperature. O.P.A. showed no hydrolysis detectable by this method in 114 hours at room temperature, but slight hydrolysis (less than 3%) of di-O.P.A. in 22 hours at 58° C.

The hydrolysis of O.P.A. in 0.1 N HCl at about 100° C. was also studied. The organic extractant was refluxed with the HCl and samples of the aqueous phase were removed from time to time and analyzed for H_3PO_4 by the vanado-molybdate method. It was found that the concentration of H_3PO_4 in the aqueous phase increased approximately linearly with time. After 250 hours, titration of the organic indicated that the O.P.A. was not completely hydrolyzed.

Settling Rate and Entrainment

The rate of settling of mixtures of alkyl phosphoric acids in diluent and Company A phosphoric acid was studied in considerable detail. When these mixtures are allowed to settle, there are two distinct breaks. The primary, visual break, that is, the rate at which a sharp interface forms, is quite rapid; the secondary break, which involves the settling of a fine mist of organic dispersed in the aqueous phase, is extremely slow. The settling rate associated with the primary break was measured as a function of volume ratio of organic to aqueous phase with several alkyl phosphoric acids. In all cases it was found to have a maximum value at a volume ratio of about

0.2. It was also found to decrease as the concentration of extractant in the diluent increased. As the temperature was increased, the time required for the primary break decreased approximately linearly. Thus a rise in temperature of 30° C. decreased the primary break-time by about half.

The settling rate associated with the primary break and the primary-break time are, however, not directly useful for design purposes as they involve a combination of the true settling rate and the rate of coalescence of the discontinuous phase after the droplets have settled to the interface. This latter rate is called the emulsion-break rate. The settling rate of the droplets is a function of their size. As there is a distribution of particle sizes in the mixture, there is a distribution of settling rates. The total amount of entrained phase after a given settling time and for a given height of liquid can be related to the distribution of settling rates.

Measurements were made of the amount of entrainment at various settling times in a settling tube. At the same time measurements were made of the emulsion-break rate. The solutions were mixed by a motor-driven stirrer in a baffled beaker and the mixture was withdrawn from the bottom of the beaker into a settling tube. After a given settling time a portion was withdrawn from the bottom of the tube, the kerosene was distilled from the sample, and the volume measured. These measurements were made at one degree of agitation only. The agitation used was quite vigorous. The results for other degrees of agitation would not necessarily be the same as the character of the emulsion is different when the intensity of agitation is varied.

It was found that entrainment losses of organic into acid decreased with increasing phase ratio of organic to acid when the acid was the continuous phase. When sufficient organic was used to make the organic phase continuous, the organic mist in the acid could not be seen at any phase ratio tested. However, a certain amount of entrainment was present at all reasonable design-settling rates.

The emulsion-break rate was found to be relatively independent of emulsion height or phase ratio, but to be dependent on area alone. When the organic phase was continuous, the emulsion-break rate was about twice as fast as when the acid phase was continuous. Comparing the values of settling rate and emulsion break rate, it appears that the settling rate is the limiting factor in the design of the settler as long as the phase ratio of organic to acid is 1:10 or lower. When the organic phase is continuous, the emulsion break rate is the limiting factor.

Similar experiments were performed at elevated temperatures. It was found that both settling rate and emulsion-break rate were much faster at the higher temperatures.

For optimum settler design the effect of entrainment on the extraction in a countercurrent system must be evaluated. Equations have been derived which relate these effects.

Effect of Light on O.P.A.

A sample of O.P.A. which had been exposed to daylight and fluorescent light for three weeks was compared with a sample which had been kept in a dark bottle since it was received. Extractions of uranium from Company A acid with both samples showed identical results. However, a sample exposed to light from an ultraviolet lamp for two days had an extraction coefficient about 30% lower than that for the untreated sample.

Effect of Heat on O.P.A.

A 10% solution of O.P.A. in kerosene was refluxed at 185° C. for one hour. The mixture darkened and upon cooling formed a second phase. Both titration and extraction experiments indicated that the O.P.A. was partially decomposed. A sample of O.P.A. was kept at 70° C. for two days. The extraction coefficient dropped to half that of untreated O.P.A.

Effect of Oxidizing Agents in O.P.A.

A sample of O.P.A. was bubbled with air for two days. The extraction coefficient dropped about 30%. Treatment of a sample with a few drops of H_2O_2 had a slightly greater effect.

Alkyl Pyro-phosphoric Acids

Extraction of Uranium

It was postulated that the increased extraction obtained by treatment of O.P.A. with P_2O_5 might be due to formation of alkyl pyro-phosphoric acids. Hence extraction experiments were performed with commercial alkyl pyro-phosphoric acids and with preparations of alkyl pyro-phosphoric acids made in the laboratory. In all cases it was found that the distribution coefficients were of a higher order of magnitude than those obtained with ortho-phosphates. Compounds of various chain lengths from butyl to decyl were tested. The extraction increased with the chain length from butyl to octyl. Nonyl and decyl gave about the same extraction as octyl. Octyl pyro-phosphoric acid was chosen for more extensive testing because octanol is cheap and easily obtainable.

Higher extractions were obtained with laboratory preparations of O.P.P.A. than with the commercial samples. Preparations made from octanol-1 from two different sources gave identical results. A preparation made from octanol-2 (capryl alcohol) showed no significant difference in extracting ability from those made with octanol-1.

As the distribution coefficient is much higher with O.P.P.A. than with O.P.A., a more dilute solution of extractant can be used. This results in a quite concentrated solution of uranium in the extractant. This concentration seems to approach a saturation value, thus giving a curved isotherm. As was shown previously, two values can be obtained from these curved isotherms, K^A_{max}, the maximum value of the distribution coefficient and C^A_{max}, the saturation concentration of uranium in the extractant.

The distribution coefficient is a function of the oxidation potential of the acid. Figure 3 is a semi-logarithmic plot of K^A_{max} vs. e.m.f. for Company A acid with a given preparation of O.P.P.A. This particular lot of O.P.P.A. is neither the poorest that has been prepared nor the best, so while this plot shows how the coefficient will vary with e.m.f. of the acid, the actual magnitude of the coefficient will change somewhat as the conditions of preparation of the O.P.P.A. are changed. Plots of K^A vs. e.m.f. for Victor O.P.A -kerosene solutions are also shown in Figure 3 for comparison.

It will be noted that, while the distribution coefficients were too low, when O.P.A. was used, to permit economical extraction of uranium from unreduced Company A acid, the coefficient with O.P.P.A. is sufficiently high to allow this. Thus with Lot 2 acid (-0.27 Volts, Pt vs. S.C.E.) the value of K^A_{max} is about 700 indicating that K_D for a 2% solution would be 14. This would result in 58% recovery for one stage or 90% for four stages if an organic to acid flow rate ratio of 1:10 were used.

The effect of the diluent used with O.P.P.A. was studied. The extractions obtained with 1% solutions of O.P.P.A. in a number of solvents were compared. Kerosene and Stoddard solvent gave the best extraction. $CHCl_3$ gave the poorest of those tested. Diesel oil was only slightly poorer than kerosene. Samples of kerosene and diesel oil were purified by removing the unsaturates with H_2SO_4. Poorer extractions resulted when these purified samples were used as diluents for O.P.P.A.

Extractions with solutions of various concentrations, from 1 to 10% O.P.P.A. in kerosene, obtained from points on the lower, nearly linear, portion of the isotherm, indicated that K_D was a linear function of concentration of O.P.P.A. and thus K^A_{max} was a constant with dilution of the extractant in this range.

Separation of Components

Attempts have been made to separate O.P.P.A. preparations into the constituent compounds by means of ion exchange and silica jel chromatography, and by liquid-liquid extraction. The results, so far, indicate that this may be possible, but complete separations have not yet been accomplished.

Decomposition with Time

The decomposition of a sample of 2% O.P.P.A. in kerosene at room temperature was studied by titrating aliquots of the solution from time to time. The titer of the solution increased throughout the entire period of 43 days. The titration curves indicated that the increase was mainly in the amount of weak acid. The increased weak acid content was evidently soluble in kerosene as the titer of aqueous washes of the solutions decreased with time.

The experiment was repeated with a sample of 2% O.P.P.A. in kerosene which was first washed with 3 M NaCl solution. In this case there was no increase in titer with time.

The effect of time at room temperature was also studied by means of single-stage extractions of uranium from Company A acid. It was found that the extraction coefficient declined with time whether the O.P.P.A. was stored in the undiluted form or diluted with kerosene. However, samples of O.P.P.A. stored at about 0° C. did not show any appreciable change with time.

Since O.P.P.A. seems to decline in effectiveness with time, it is recommended that when possible it be prepared immediately before use. Extractions made within a few hours after preparation indicate that the decline in extracting ability is not apparent up to five hours from the time of preparation.

Degradation at Elevated Temperatures

O.P.P.A. solutions were heated to 70° C. for various lengths of time. A viscous phase separated from a 1% solution in kerosene after 30 minutes and from a 20% solution in two to three hours. The appearance of the viscous phase was accompanied by a considerable drop in the extraction coefficient with Company A acid. Decyl pyro-phosphoric acid solutions, when heated, did not form a viscous phase. The extraction coefficient decreased with time of heating but the effect seemed to be less than in the case of O.P.P.A.

O.P.P.A. solutions were stirred with Company A phosphoric acid at 70° C. for various lengths of time, allowed to cool and stirred again. The extraction coefficients indicated that considerable degradation had taken place. The coefficient decreased 95% in 30 minutes stirring time.

These experiments indicate that the extractant should be cooled as soon as possible after preparation and stored at as low a temperature as possible.

Solubility

The solubility of O.P.P.A. in water has not been determined, but it is probably of about the same magnitude as the solubility of O.P.A. It was found, however, that a water wash of a fresh O.P.P.A.-kerosene solution removed some of the acidity. The kerosene phase when it was titrated several days after washing had increased in acidity, but the titer of the water wash remained the same. This indicates that the components which dissolved in the water were free phosphoric acid and mono-O.P.A. The increase in titer of the organic phase thereafter is an indication of hydrolysis.

Hydrolysis

The rate of hydrolysis of O.P.P.A. when it was refluxed at about 100° C. with water and HCl solutions was studied by measurement of the increase in H_3PO_4 content of the aqueous phase. The H_3PO_4 was measured by the vanado-molybdate method. The curves of H_3PO_4 concentration vs. time were similar and showed a rapid rate of hydrolysis for the first five to ten minutes, a moderate rate for the next 30 to 60 minutes and then a very slow constant rate which continued to the end of the run. It seemed probable that the hydrolysis of pyro-, poly-, and meta- phosphates to ortho-phosphate was complete at the point where the slow constant rate began and that thereafter the hydrolysis of ortho-phosphate was being measured. The approximate times for this hydrolysis at 100° C. for water, 0.1 N HCl and 1 N HCl were respectively 55, 45 and 32 minutes.

The rate of hydrolysis of a 10% solution of O.P.P.A. in kerosene with 0.1 N HCl solution was measured in the same manner and found to be slightly slower. The temperature, however, was only 90° C. The time of hydrolysis for a 10% solution of O.P.P.A. in isopropyl ether with 0.1 N HCl was 3 3/4 to 4 hours. The temperature in this case was 61° C. The slower rate is probably due to the lower temperature rather than to the solvent. The time required for hydrolysis with 0.1 N HCl of the undiluted O.P.P.A. to ortho-phosphate at room temperature was 22 hours.

From the above studies it was determined that for analytical purposes, the optimum conditions for hydrolysis of O.P.P.A. to O.P.A. are 100° C. with 0.1 N HCl for 45 to 60 minutes.

A study of the hydrolysis of O.P.P.A. as a function of pH indicated that the hydrolysis is most rapid in acid solutions. Above pH 6 the rate of hydrolysis does not seem to vary greatly with pH but the hydrolysis is still appreciable.

Settling Rate

The settling rates of a mixture of 1% O.P.P.A. in kerosene and Company A acid were determined at 20° C. The data was almost identical to that obtained with a 10% O.P.A.-kerosene solution.

Extraction of Uranium with Miscellaneous Preparations

An attempt was made to prepare an alkyl pyro-phosphate by adding diisobutl carbinol to a kerosene slurry of P_2O_5 but this resulted in a substance insoluble in kerosene. Diamyl pyro-phosphoric acid, prepared by adding n-amyl alcohol to a P_2O_5-kerosene slurry, was also insoluble.

Preparations were made by using n-octyl alcohol with a kerosene slurry of P_2O_5 with a P_2O_5-alcohol mole ratio of 1:1. The products formed were not soluble in either kerosene or benzene. Extraction coefficients, obtained with Company A acid, were lower than those obtained with O.P.P.A. solutions. It is not known whether these preparations contain poly-phosphates or poly-meta-phosphates.

Attempts were made to prepare O.P.P.A. by reacting octanol with pyro-phosphoric acid. However, the resulting extraction coefficients were poor. Attempts to make alkyl phosphonic acids have also resulted in products with low coefficients.

Conclusions

The following conclusions can be drawn from the study of extractants.

Uranium can be effectively extracted from phosphoric acids with alkyl ortho-phosphoric acids and alkyl pyro-phosphoric acids dissolved in organic solvents. All other compounds tested have proved less effective.

Preparation

Alkyl ortho-phosphates and pyro-phosphates are prepared by the reaction of P_2O_5 with alcohol. For the preparation of pyro-phosphates the best method is to slurry the P_2O_5 with kerosene and add the alcohol to the slurry. The optimum concentration

of the slurry is 0.1 to 0.2 g. P_2O_5 per ml. of kerosene. The optimum ratio of alcohol to P_2O_5 is 2:1.

Extraction with Alkyl Ortho-phosphoric Acids

The maximum extraction coefficient is obtained with a mole ratio of 2 di- to 1 mono- ortho-phosphoric acid.

The effectiveness of ortho-phosphoric acids depends on the chain length. There is a maximum with amyl on a weight basis, but as amyl phosphoric acid is fairly soluble in phosphoric acid, octyl phosphoric acid is believed to be superior.

The effectiveness of ortho-phosphoric acids increases with increasing branching in the carbon chain.

The distribution coefficient obtained with O.P.A. can be increased by addition of P_2O_5.

Kerosene has been found to be a satisfactory diluent for these extractants.

K_D for alkyl ortho-phosphoric acids is a linear function of the concentration of the extractant in the diluent.

O.P.A. can be separated into mono- and di- fractions by partition between selected immiscible solvents.

The distribution loss of mono-O.P.A. in water is about 3.9 g./l.; in C.P. 40% H_3PO_4 it is about 1 g./l.; in Company A acid it is about 0.3 g./l. No solubility of di-O.P.A. has been detected.

O.P.A. can be hydrolized at elevated temperatures with HCl solutions, but the hydrolysis is very slow.

Settling rates and emulsion-break rates have been determined for O.P.A.-kerosene, Company A mixtures. The settling rate is the limiting factor in design of the settler as long as the phase ratio of organic to acid is 1:10 or less. The emulsion-break rate is the limiting factor when the organic phase is continuous. Both settling rates and emulsion-break rates increase with temperature. Inability to define degree of mixing limits the usefulness of this study.

Heat, ultraviolet light, and oxidizing agents all lower the effectiveness of O.P.A.

Extraction with Alkyl Pyro-phosphoric Acids

Distribution coefficients with pyro-phosphates are of a higher order of magnitude than those with ortho-phosphates. Attempts to make preparations with higher P_2O_5 content have not so far given extractants superior to O.P.P.A.

The effectiveness of alkyl pyro-phosphoric acids increases with length of the carbon chain. For this reason, and because the solubility of these compounds decreases with increasing chain length, most of the studies have been with octyl pyro-phosphoric acid.

Alkyl pyro-phosphates freshly prepared in the laboratory extract uranium better than commercial preparations.

The distribution coefficient is a function of oxidation potential of the acid as in the case of O.P.A., but since the magnitude is greater, extraction of uranium from the acid without reduction is feasable.

Kerosene is a satisfactory diluent for O.P.P.A. solution.

The effectiveness of O.P.P.A. preparations decreases with time. The rate of degradation was greater when the solutions were stored at elevated temperatures. O.P.P.A. is hydrolyzed to O.P.A. by HCl solutions in 30 - 60 minutes at 100^{b} C. At room temperature the hydrolysis requires about 22 hours. Hydrolysis is slower with basic solutions, but is still appreciable.

A 1% O.P.P.A.-kerosene solution has about the same settling rate as a 10% O.P.A.-kerosene solution.

D. Extraction of Uranium with Multistage Countercurrent Units

Extraction by a multistage countercurrent system results in a more complete recovery from the acid than in a single-stage, a higher concentration of U_3O_8 in the organic effluent, and a lower amount of extractant required per pound of recovered U_3O_8. As all these factors tend to reduce the cost of the process, a program was initiated to build such systems and study their operation.

A simulated multistage countercurrent system, consisting of a set of separatory funnels, was first set-up to determine if such a process would operate in this case. The method described in Perry[2] was used. The results showed that there was a definite advantage to multistage operation and that, within the experimental error, the data checked with results predicted from theoretical calculations.

A countercurrent spray column was constructed and runs were made, at various flow-rate ratios, with butyl phosphoric acid, benzene solutions, and Company A acid. The data indicated that a 30-inch column resulted in extractions equivalent to two to three theoretical stages. Thus the height equivalent to a theoretical stage for this column was about one foot.

A small Scheibel column was built with six impellers. Settling sections between them were packed with saran filament. The best run with this column resulted in extraction equivalent to three theoretical stages.

A four-stage box-type mixer-settler of the type described by Morello and Poffenberger[3] was constructed. Considerable difficulty was encountered with this apparatus due to back mixing of organic, i. e., part of the organic phase being carried in the reverse direction by the aqueous phase, unstable interface levels, and the long time necessary to reach equilibrium. In all cases the recovery was less than that predicted for four theoretical stages. It was concluded that for successful operation there must be better control of flow between stages.

A four-stage mixer-settler with separated stages was constructed from Florence flasks equipped with extra inlets and outlets. Mixer and settler vessels of improved design were later substituted for the Florence flasks. The acid and organic phases were fed into the system by constant volume metering pumps, and interstage flow was partly by gravity and partly by pneumatic lifts. Figure 4 is a diagram of the apparatus. The dotted lines in the figure indicate organic flow. The heavy lines indicate acid flow.

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2 Perry, J. H., CHEMICAL ENGINEERS' HANDBOOK, (2nd ed.; McGraw-Hill Book Company, Inc., New York and London, 1941), p. 1219.
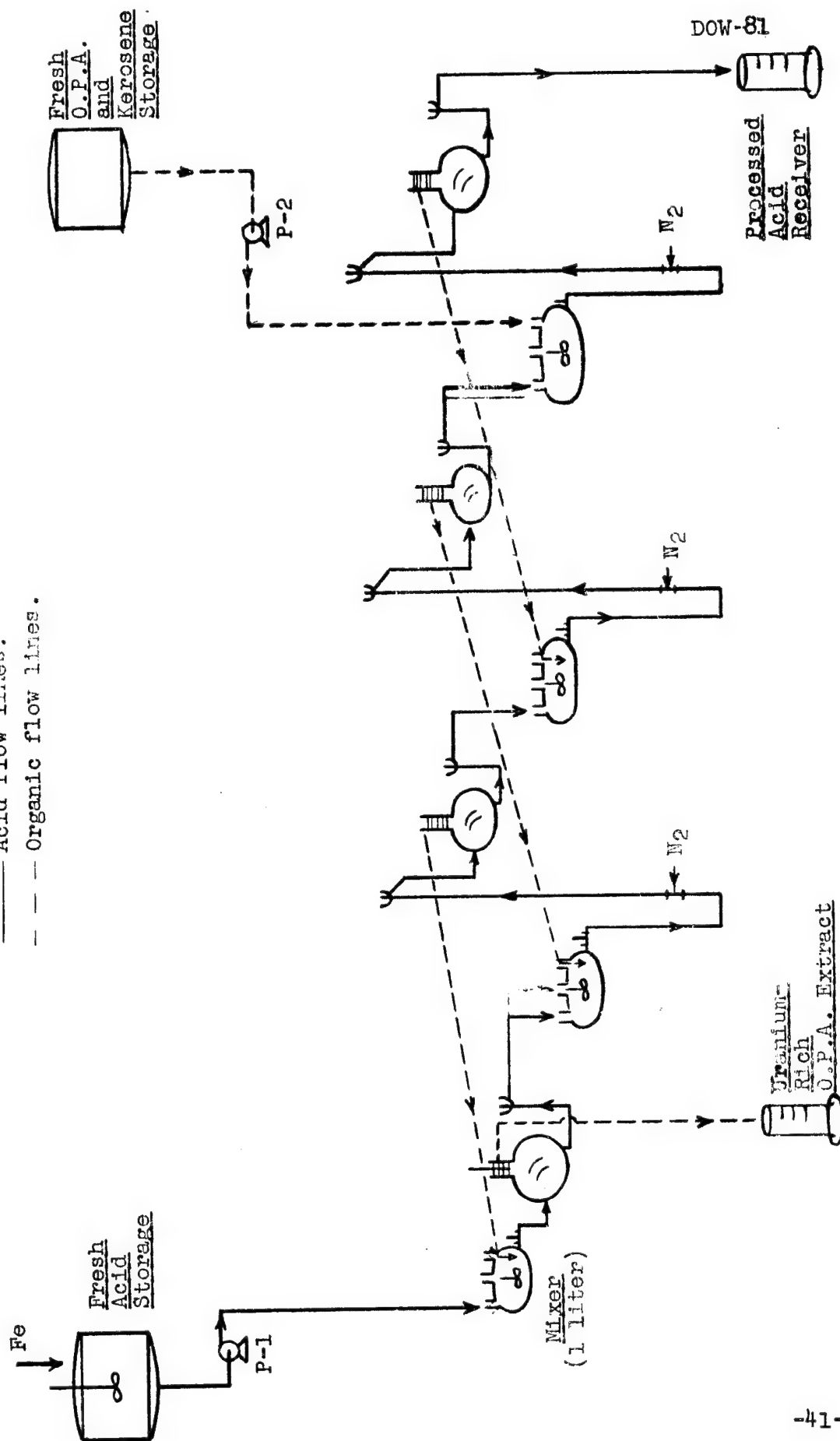3 Morello, V. S., and Poffenberger, N., Ind. Eng. Chem. 42, 1021-35 (1950).

Figure 1. Laboratory-Scale Four-Stage Mixer-Settler.

Continuous countercurrent operation.

——— Acid flow lines.
– – – Organic flow lines.

Fresh O.P.A. and Kerosene Storage

DOW-81

Processed Acid Receiver

P-2

N_2

N_2

N_2

Uranium-Rich O.P.A. Extract

Mixer (1 liter)

Fresh Acid Storage

Fe

P-1

The system was first run with 10% O.P.A.-kerosene and re-
duced Company A acid. Runs were made with two, three, and four
stages. Very good agreement with the theoretical recoveries, pre-
dicted from the graph in Figure 2, was found. Thus with K_D equal
to 20, at a flow-rate ratio of 16:1, nearly 90% recovery was at-
tained. The effluent extractant contained approximately 1.5 grams
U_3O_8 per liter.

Studies were made in which the O.P.A.-kerosene solutions
were recycled in the countercurrent mixer-settler unit after pre-
cipitation of the uranium from the organic with HF. As was found
with single-stage extractions, the extraction showed a sharp drop
between the first and second use and a slower drop thereafter.
Another recycle run was made in which P_2O_5 was added to the O.P.A.-
kerosene after precipitation of the uranium. The run was continued
for seven cycles. The recovery of uranium in this case did not
decrease, but remained well over 90% in each cycle.

The reagent requirements for uranium recovery calculated
from this run would be nine pounds of O.P.A. and seven pounds of
P_2O_5 per pound U_3O_8, assuming no loss of kerosene.

Runs were also made with this apparatus using O.P.P.A.-
kerosene solutions as the extractant. The higher extraction co-
efficients of O.P.P.A. compared to O.P.A. make it possible to use
more dilute solutions. This reduces the loss of extractant by
entrainment and lowers the HF consumption during the precipitation
because of lower solubility of HF in the organic.

With reduced Company A acid, it was found that a 1%
O.P.P.A. solution with a flow-rate ratio of 10:1 (acid:organic)
or a 2% O.P.P.A. solution with a flow-rate ratio of 16:1, would
give greater than 90% recovery from the acid in two stages at
room temperature. A two-stage run with preheated acid (effluent
temperature 50° C.) with 1% O.P.P.A. at a flow ratio of 10:1
gave approximately 15% poorer recovery.

When Company A acid is not reduced, the distribution co-
efficient for uranium is still great enough for extraction if
O.P.P.A. is used. Using unreduced acid (e.m.f. -0.22 v., Pt vs.
S.C.E.) and an O.P.P.A. preparation made by direct addition of
P_2O_5 to the alcohol, 55% recovery was obtained after four stages
with a 1% solution at a flow-rate ratio of 10:1, 80% with 2%
O.P.P.A. at 10:1, and greater than 90% with 5% O.P.P.A. at 16:1.
Better results were obtained with an O.P.P.A. preparation made
by adding alcohol to a kerosene slurry of P_2O_5. In this case
90% recovery was obtained with 2% O.P.P.A. at a flow-rate ratio
of 10:1 at room temperature. In the case of unreduced acid,
four stages were required for recoveries over 90%, while with
reduced acid this recovery could be obtained with two stages
using 2% O.P.P.A. or in four stages with 1% O.P.P.A.

The entrainment of organic in the effluent acid in this system was measured for a typical four-stage run with a flow-rate ratio of 16:1. It was found that 1% to 3% of the feed organic was entrained. A settler was built for the fourth stage designed so that the organic could be fed back into the fourth-stage mixer, so that in this mixer the organic could be maintained as the continuous phase. In this manner the entrainment was lowered to 0.6% of the feed organic.

In these runs, mixing times of about four minutes and settling times of five minutes per stage were used most commonly.

Conclusions

The following conclusions can be drawn from the study of multistage mixer-settler operation.

1. High stage efficiencies were obtained with a mixer-settler with separated stages. Operational difficulties were encountered with box-type mixer-settlers and column extractors.

2. Flow-rate ratio, extractant concentration, and reduction of acid were varied with both O.P.A. and O.P.P.A. The recoveries obtained were of the magnitude predicted by the single-stage extraction studies.

E. Recovery of Uranium from Organic Extractants

From Alkyl Ortho-phosphoric Acids

Analysis

The following analysis is typical of a 10% O.P.A.-kerosene phase after a single-stage extraction of uranium from Company A acid.

	From unreduced acid:	From reduced acid:
U_3O_8	300 mg./l.	800 mg./l.
Fe	1.0 g./l.	.45 g./l.
Al	.03 g./l.	.04 g./l.
Ca	.03 g./l.	0 g./l.

Besides uranium, only iron was extracted to an appreciable extent.

Precipitation with HF

Uranium was precipitated from butyl, amyl, and octyl ortho-phosphoric acid extracts with aqueous HF solutions. The amount of HF required depended on the concentration of uranium in the organic, the concentration of extractant in the organic, and the amount of impurities in the organic. The organic solution was shaken with HF and the uranium formed a green precipitate in the aqueous phase. Overall recoveries of up to 99% were obtained in these precipitations.

A number of precipitation experiments were performed with a synthetic extract made by dissolving uranous salts in a 10% solution of O.P.A. in kerosene. These experiments were done in polyethylene equipment. A series of precipitations were made with various concentrations of HF. Volume ratios of organic phase to aqueous phase of 1:1 and 10:1 were used. With the 1:1 phase ratio, stable emulsions were formed when solutions containing less than 10% HF were used. With the 10:1 phase ratio, emulsions were still formed at low HF concentrations, but they were not as stable.

The final concentrations of uranium in both organic and aqueous phases were measured. The concentration in the organic decreased with increasing HF concentration over the entire range studied. The concentration in the organic was slightly higher with the 10:1 ratio than with the 1:1 ratio.

The concentration in the aqueous phase, however, increased with HF concentration. In the case of the 1:1 ratio, there was a maximum at about 30% HF, but with the 10:1 phase ratio the uranium concentration in the organic continued to increase over the range studied.

A series of precipitations was made with 48% HF in which the phase ratio of organic to aqueous phase was varied from 110 to 0.6. It was found that as the phase ratio increased, the recovery of uranium increased, although the concentration of dissolved uranium in both phases also increased. This is because the greatest loss in uranium is to the aqueous phase and hence, decreasing the aqueous volume increases the recovery.

A study of the time of shaking necessary for the precipitation indicated that the time was not critical, but that any period over one minute was adequate.

A series of precipitations was made in which solutions of HF were added to the O.P.A.-kerosene extract in the presence of concentrated phosphoric acid. It was found that precipitation of 80% to 85% of the uranium could be obtained with less HF than by addition of HF alone. A search was made for a substitute for phosphoric acid, but no other compound was found which would reduce the amount of HF required. As the precipitate obtained in this may seem to be a uranous phosphate, containing little fluoride, a search was made for a substitute for HF to be used with concentrated phosphoric acid, but none was found which would precipitate the uranium.

Attempts were made to precipitate uranium from the O.P.A.-kerosene solutions with gaseous HF. Precipitation by this method was slow, but was 99.8% complete in four hours. However, there was evidence that the extractant had deteriorated. Titration showed that 95% of the titratable hydrogen was lost.

Attempts were made to precipitate uranium from these solutions with sodium and ammonium fluorides, but no uranium precipitates were obtained. The effect of addition of sodium ion to HF was also studied. It was found that as the concentration of sodium ion increased, the concentration of uranium in the aqueous phase decreased, but the concentration of uranium in the organic phase increased. Thus there was little change in overall recovery.

These results provide a plausible explanation for a discrepancy between the results of precipitations with HF from actual extracts and from synthetic extracts. The concentration of uranium in the aqueous phase is much lower in the case of actual extracts than in the case of synthetic extracts. This may be due to the other ions which were extracted.

A study has been made of the effect of HF on the O.P.A.-kerosene solutions. It was found that treatment with HF has a deleterious effect on subsequent extraction of uranium from phosphoric acid. A series of O.P.A.-kerosene samples were treated with various concentrations of HF for various times. Titration of these samples with NaOH and analysis of the aqueous phase for free H_3PO_4 indicates that HF causes hydrolysis to take place. It was found that essentially all of the O.P.A. is hydrolyzed to H_3PO_4 in 60 hours. The mono-O.P.A. hydrolyzes faster than the di-O.P.A. Octanol could be detected by odor in menthanol extracts of the hydrolyzed samples. Some fluoride was dissolved in the organic phase, but most of this could be removed by washing with water.

Re-extraction with Concentrated Phosphoric Acid

It has been shown that the distribution coefficient of uranium between phosphoric acid and alkyl ortho-phosphates decreases as the concentration of phosphate in the aqueous phase increases. Thus with high concentrations of phosphoric acid, the value of the coefficient becomes less than one and the distribution favors the aqueous phase. The distribution coefficient of U IV between a 10% O.P.A.-kerosene solution and 68% H_3PO_4 was found to be about one. With 85% H_3PO_4, it was approximately , this is, 7 in favor of the aqueous phase. When the uraniu n the organic was oxidized with a few drops of H_2O_2, the coefficient into the aqueous phase was approximately doubled.

The distribution loss of O.P.A. into 85% H_3PO_4 was determined to be about 0.51 gram di-O.P.A. and 0.26 gram mono-O.P.A. per liter of 85% H_3PO_4. The hydrolysis of O.P.A. in 85% H_3PO_4 at room temperature was found to be less than 10% in twenty hours.

Uranium was recovered from the 85% H_3PO_4 solutions by two methods: dilution and direct precipitation with HF; and dilution, re-extraction with O.P.A.-kerosene, and precipitation with HF. The best recovery obtained by the first method was approximately 70% from 20% H_3PO_4. Over 90% recovery was obtained by the second method when the acid was diluted to 26.5% H_3PO_4 and re-extracted with 10% O.P.A. in kerosene.

Re-extraction with Concentrated HCl

Uranium can be extracted from alkyl phosphoric acid solutions by use of concentrated HCl solutions. The distribution coefficient for uranium between 20% O.P.A.-kerosene and 11.7 M HCl was found to be 1.6 into the aqueous phase. When the organic solution was oxidized by the addition of H_2O_2, the extraction coefficient was 2.2 into the aqueous phase. An extraction, using a Scheibel column, produced a HCl solution containing 2.7 grams U_3O_8 per liter.

As extraction with both concentrated H_3PO_4 and concentrated HCl is improved by oxidation of the uranium, a study was made of this oxidation. It was found that stoichiometric amounts of H_2O_2, $KMnO_4$, or $NaClO_2$ would oxidize U IV to U VI entirely, but that Cl_2, either as a gas or in solution, would not give complete oxidation.

The solubility of O.P.A. in concentrated HCl was found to be about 0.6 gram mono-O.P.A. per liter HCl. No detectable amount of di-O.P.A. was dissolved. When the same sample of HCl was re-used after removal of uranium by ion exchange, the amount of O.P.A. lost to the HCl decreased with each cycle.

The solubility of HCl in O.P.A.-kerosene solutions was found to be about 12 grams HCl per liter. The dissolved HCl could be entirely removed, within experimental error, by one wash with water.

Uranium was recovered from the HCl solutions by two methods: ion exchange; and distillation. The ion-exchange procedure consisted of passing the solutions through a 7 mm by 42 mm column of Dowex 1. The uranium was adsorbed on the resin with a breakthrough loading value of 62.5 mg. U_3O_8/ml. resin. The uranium was eluted with water with a peak concentration of 105 grams U_3O_8/liter and was precipitated with ammonia. The distillation procedure consisted of distilling the HCl from the solution and leaving the uranium in the residue.

Miscellaneous Methods of Uranium Recovery

Uranium was recovered from alkyl ortho-phosphoric acid solutions in several other ways. Precipitation with ammonia gave essentially complete precipitation of uranium, but it was necessary to neutralize the first hydrogen of the O.P.A. When O.P.A.-kerosene solutions were shaken with methanol, most of the O.P.A. was extracted into the methanol. The uranium left in the kerosene was then precipitated by ammonia or HF solutions. However, methanol extracts mono-O.P.A. better than di-O.P.A. and thus the extractant is altered in this process.

A number of methods were tried which gave only partial recovery of uranium. Among these were precipitation with aniline, extraction with sodium pyro-phosphate, extraction with sodium poly-phosphate, and extraction with sodium oxalate.

The following methods were tested for recovery of uranium from alkyl ortho-phosphoric acid solutions, but failed to give satisfactory recovery.

Adsorption on activated carbon.
Adsorption on anion and cation resins.
Freezing.
Evaporation.
Electrolytic reduction.
Treatment with H_2S.
    "   " K_2CO_3.
    "   " $H_2Si_2F_6$.
    "   "   Cryolite.
    "   "   hexamethylene tetramine.
    "   "   3-fluosalicylaldehyde.
    "   "   thenoyltrifluoracetone.
    "   "   pyridine.
    "   "   sodium benzene sulfonate.
    "   "   sodium benzene disulfonate.
    "   "   ethylenediamine tetraacetic acid.
    "   "   tartaric acid.
    "   "   citric acid.
    "   "   oxalic acid.
    "   "   pentaerithritol.
    "   "   tetraethylene glycol.
    "   " NH_4Cl.
    "   " $CaCl_2$.
    "   " $K_4Fe(CN)_6$

From Octyl Pyro-phosphoric Acid

Analysis

The following analysis is typical of O.P.P.A.-kerosene solutions after extraction of uranium from Company A acid in a multistage mixer-settler at room temperature.

U_3O_8 0.7 g./l.
Fe   0.7 g./l. (if extraction is from unreduced acid)
        0.2 g./l. (if extraction is from reduced acid)

Only uranium and iron have been found to be appreciably extracted by these solutions. The uranium in the extract has been found to be U IV whether the extraction was from reduced or from unreduced acid.

Precipitation with HF

Uranium can be recovered from O.P.P.A.-kerosene solutions by precipitation with HF. The amount of HF required is less than that necessary for precipitation from O.P.A.-kerosene solutions. Thus, up to 99% of the uranium contained in a 1% O.P.P.A.-kerosene solution has been precipitated with 1.25 pounds of HF per pound of contained U_3O_8.

Precipitations were attempted with various concentrations of HF. A green precipitate was obtained with all concentrations above 3%. However, a stable emulsion formed in the aqueous phase when concentrations of HF below 20% were used. Increasing HF concentrations, in the aqueous phase, results in decreasing uranium concentration in the organic phase. A substantial amount of uranium is dissolved in the aqueous phase at all HF concentrations measured, but the maximum solubility is in 35% HF. This loss could probably be eliminated by re-use of the aqueous phase. Use of 60% HF results in a dark purple color in the organic phase, which probably indicates a greater degradation of the extractant than when lower HF concentrations were used.

The time of contact with HF, necessary for precipitation, is very short. The shortest time used, as yet, was fifteen seconds for mixing and one minute for settling. The precipitation should be done as rapidly as possible as the amount of degradation of the extractant is a function of the time of contact with HF.

It has been found that treatment of an O.P.P.A. solution with HF has a much greater deleterious effect on further extraction of uranium from phosphoric acid than was found with O.P.A. solutions. Solutions of O.P.P.A. are hydrolyzed by HF solutions quite rapidly. For this reason the time of treatment with HF should be as short as possible and the extractant should be re-used as soon as possible after precipitation. Precipitation with anhydrous HF was slow and resulted in much greater degradation of the extractant than was found when aqueous HF solutions were used.

Re-extraction of Uranium with Concentrated H_3PO_4

The distribution coefficient for uranium between 1% O.P.P.A. in kerosene and 85% H_3PO_4 was found to be approximately five in the direction of the organic. Thus uranium cannot be easily extracted from O.P.P.A. solutions by this method.

Precipitation of Uranium by Treatment with Alcohol

When O.P.P.A.-kerosene extracts containing uranium are shaken with alcohol, uranium precipitates as a gelatinous green solid. It is believed that this precipitation is the result of the organic phosphoric acid being preferentially extracted by the alcohol. The organic phosphate-uranium compound is not soluble in kerosene alone without O.P.P.A. and hence it precipitates. The O.P.P.A. can be recovered from the methanol by dilution with water and re-extraction with kerosene. This method of uranium recovery might be difficult to handle on a large scale because the precipitate is difficult to filter, and the kerosene and alcohol have nearly the same density and hence are difficult to separate.

Analysis of Precipitates

A number of the precipitates obtained by HF treatment of alkyl ortho-phosphoric acids and O.P.P.A. have been analyzed. The following are analyses of typical precipitates which were dried at $100°$ C.

(1) A precipitate from an amyl ortho-phosphoric acid solution.
(2) A precipitate from a butyl ortho-phosphoric acid solution.
(3) A precipitate from an octyl ortho-phosphoric acid solution.
(4) A precipitate from an O.P.P.A. extraction of reduced acid.
(5) A precipitate from an O.P.P.A. extraction of unreduced acid.

	(1)	(2)	(3)	(4)	(5)
	(All figures in per cent)				
U_3O_8	15.1	26.0	35.8	64.5	50.3
F^-	19.7	26.0	----	25.8	22.4
PO_4	15.2	15.0	----	7.2	----
Fe	1.4	1.4	----	0.3	1.26
Ti^-	0.6	0.6	----	----	----
Ca	4.1	----	----	----	----
Mg	1.0	----	----	----	----
Al	2.1	----	----	0.6	0.11
Rare Earths	5.0	----	----	----	----
L.O.I.	37.0	----	----	----	----

The first analysis listed is the only complete analysis that has been made. Besides small percentages of iron, titanium, calcium, magnesium, and aluminum, about 5% of rare earths were also found. Spectrographic analysis showed La, Y, Yb, and others, but no Ce.

Samples (4) and (5) show the difference in precipitation obtained from O.P.P.A. extracts of reduced and unreduced acid. A higher concentration of iron and a lower concentration of uranium is obtained from the unreduced acid. However, the precipitates from the O.P.P.A. solutions are very similar to those from O.P.A. solutions.

Conclusions

The following conclusions can be drawn from the study of the recovery of uranium from organic extractants.

Recovery from Alkyl Ortho-phosphoric Acids

1. Uranium can be precipitated from alkyl ortho-phosphoric acid by addition of HF solutions.

2. Less HF is required if the HF is added in the presence of concentrated phosphoric acid.

3. Precipitation with fluoride salts has not been successful.

4. It has been determined that HF accelerates the hydrolysis of O.P.A. solutions.

5. Uranium can be extracted from alkyl ortho-phosphoric acid solutions with concentrated phosphoric acid. It can best be recovered from this solution by dilution and re-extraction with a smaller volume of alkyl ortho-phosphoric acid.

6. Uranium can be extracted from alkyl ortho-phosphoric acid solutions with concentrated HCl. It can best be recovered from the HCl by ion exchange. Alkyl ortho-phosphoric acids are partially soluble in HCl.

Recovery from Alkyl Pyro-phosphoric Acids

1. Uranium can be recovered from octyl pyro-phosphoric acid by precipitation with HF solutions. Up to 99% of the uranium has been precipitated with 1.25 pounds of HF per pound of U_3O_8 added as a 48% solution.

2.   Solutions of O.P.P.A. are hydrolyzed by HF solutions quite readily. Thus the time of contact with HF should be as short as possible and the extractant should be re-used as soon as possible after precipitation.

3.   Precipitates obtained with HF from ortho- or pyrophosphates are quite similar, and often contain over 50% U_3O_8.

F. Recycle and Restoration of the Extractant

Alkyl Ortho-phosphoric Acids

Recycle

An extensive study was made of the behavior of alkyl phosphoric acid solutions when the same sample was used repeatedly to extract uranium from phosphoric acid. The initial experiments were done with butyl phosphoric acid. A 50% solution was used on sixteen successive samples of unreduced Company A acid at room temperature. The uranium was not removed from the extractant between cycles. No drop in distribution coefficient was observed.

The behavior of O.P.A. solutions was studied more thoroughly. A 50% solution of O.P.A. in kerosene was used to extract uranium at room temperature from ten successive portions of a synthetic phosphoric acid solution (30% P_2O_5) to which uranium had been added. Uranium was not removed from the extractant between cycles. A plot of distribution coefficient vs. number of cycles gave an approximately straight line. The coefficient dropped to half its value in the ten cycles.

The experiment was repeated with a similar synthetic phosphoric acid to which 42 grams Na_2SO_4 had been added per liter. This simulated the sulfate concentration of Company A acid. The plot of distribution coefficient vs. number of extractions was approximately linear, but the drop in coefficient was greater than in the case without sulfate. The final value was less than one third the initial value.

Addition of 24.5 grams KF per liter acid lowered the coefficient for the first cycle to approximately 1/100 of that for the acid without fluoride.

The experiment using synthetic phosphoric acid containing only uranium was repeated and the extract was treated between cycles with aqueous HF to precipitate the uranium. There was a sharp initial drop in distribution coefficient. The value for the second cycle was only 1/20 of the value for the first cycle. The coefficient continued to drop until after eight cycles the value was about 1/300 of the initial value.

The behavior of O.P.A. solutions when recycled with Company A acid was also studied. O.P.A.-kerosene solutions were contacted with successive portions of acid. The uranium was removed between cycles by HF precipitation. The distribution coefficient showed a pronounced drop after the first use and a gradual drop thereafter. Analysis of the final organic showed fluoride and iron to be present and the concentration of O.P.A. in the solution to be slightly less than the original concentration due to hydrolysis, solubility, and handling losses.

The recycle experiment was repeated with removal of uranium between cycles by re-extraction with concentrated phosphoric acid. Both reduced and unreduced Company A acid were used. With reduced acid there was a drop in the distribution coefficient after the first cycle, but not as great a drop as was found with HF precipitation of the uranium. The coefficient then remained approximately constant from the second to the tenth cycle. With unreduced acid there was no initial drop.

The experiment was again repeated with removal of uranium between cycles by re-extraction with concentrated HCl. The distribution coefficient showed no initial drop, but a linear decline for eleven cycles was evident. The value for the eleventh cycle was about half that for the first cycle.

Restoration

The greatest decline in distribution coefficient upon recycling was found when HF solutions were used to precipitate the uranium. However, this is the simplest method yet found for removal of uranium from the organic. Hence many experiments were performed in an attempt to restore the extractant.

An obvious approach to the problem was to attempt to remove the dissolved fluoride from the organic. These attempts were based on the assumption that dissolved fluoride was interfering with the extraction, but the extractant itself had not otherwise been affected by the fluoride treatment. Washes were tried with acids, sodium silicate solution, and aluminum salts, but, while slight improvement was shown in some cases, no great improvement was found. Treatment with solids, such as gypsum, anhydrous $CaCl_2$, activated charcoal, and glass wool, had little effect. Treatment with an anion-exchange resin also had but little effect.

As it was possible that the fluoride might be chemically combined with the O.P.A., a number of heat treatments were tried. Treatment for long periods on the hot plate and treatment with steam resulted in partial restoration of the extractant.

It was thought that as some ferric iron is removed from the acid by the extractant, that the distribution coefficient might be improved if this iron were reduced before re-use of the extractant. Treatment of the extractant with zinc changed the color of the solutions, but did not appreciably improve the extraction.

Another possible explanation of the action of HF on the extractant is that it may promote hydrolysis of the O.P.A. or of any small amount of O.P.P.A. that may be present. If this were so, it would be likely that P_2O_5 would reverse this reaction. Thus experiments were performed in which 0.1 gram P_2O_5 per gram of contained O.P.A. was added to the O.P.A.-kerosene solution between cycles for seven cycles. The solution was stirred for about ten minutes and in most cases the P_2O_5 completely dis-solved. A plot of distribution coefficient vs. number of cycles showed that the extraction improved with re-use of the extractant. The results were somewhat better when the organic was washed with 60% H_3PO_4 between cycles. An experiment in which the amount of added P_2O_5 was varied indicated that 0.04 gram P_2O_5/gram of con-tained O.P.A. was sufficient to raise the distribution coeffici-ent to its initial value.

An extraction with un-used O.P.A. to which P_2O_5 had been added indicated that in this case, also, improved extraction re-sulted. This indicates that this treatment actually enhances the extractant rather than merely restoring it to its original effec-tiveness.

A sample of kerosene, recovered from six-times-old O.P.A. by extraction of the O.P.A. with concentrated H_2SO_4, was compared with fresh kerosene as a diluent for fresh O.P.A. Single-stage extractions of uranium from Company A acid gave almost identical distribution coefficients indicating that the kerosene diluent is not noticeably affected by the extraction.

Octyl Pyro-phosphoric Acid

Precipitation of uranium from O.P.P.A. solutions with HF was found to have much more effect on the extraction when the solution was re-used than was the case with O.P.A. solutions. A study of the extraction coefficient obtained on re-use of O.P.P.A. solutions, after precipitation of uranium with HF, indicates that the degradation of the extractant is a function of contact time with HF. Thus with two minutes contact, the coefficient had 1/4 the value from the first use; with one hour contact time, it had 1/14 the initial value; with 18 hours contact time, it had only 1/40 the initial value. The effect of storage time after filtration of the uranium was also studied. It was found that the extraction coefficient decreased rapidly with time of storage.

Attempts to improve the extraction by treating the deteri-orated solutions with diatomaceous earth or by washing them with 40% H_3PO_4 solutions were not successful. However, the H_3PO_4 wash slowed the rate of degradation.

Attempts were made to restore O.P.P.A. solutions, from which the uranium had been precipitated with HF, by the addition of P_2O_5. Considerable restoration was effected, but an excessive amount of P_2O_5 was required. Addition of fresh O.P.P.A. to the used solutions, however, was found to restore the extraction co-efficient to its original value. It was found that for the second use addition of fresh O.P.P.A. in the amount of 50% of the original content was sufficient to restore the solution to its original efficacy. For the third usage, only 30% make-up was required. This compares closely to the loss of O.P.A. in 30% H_3PO_4 (0.3 gram O.P.A. per liter acid), and suggests that beyond this point the addition of 30% make-up per cycle will result in a steady state of operation.

The amount of make-up required will depend on a number of factors, such as the time of contact with the acid, the tempera-ture of the acid, the time of contact with HF, and the time of storage before and after precipitation. These will probably vary with the design of the plant.

Samples of kerosene have been reclaimed from used ex-tractants by removal of the extractant and degradation products with concentrated sulfuric acid. On re-use with fresh O.P.P.A., the extraction coefficients were idential to those obtained with fresh kerosene.

Conclusions

The following conclusions can be drawn from the study of recycle and restoration of extractants.

1. Alkyl ortho-phosphoric acids gradually lose their extracting power when they are re-used after removal of uranium. This degradation is more rapid when HF is used than when the uranium is removed by re-extraction into strong acids.

2. Attempts to restore the solutions by removal of residual fluoride by various means were not very successful. Ad-dition of P_2O_5 to the extractant restored it fully. By this means an O.P.A. solution was re-used for seven cycles without significant decrease in the extraction coefficient.

3. The loss in extracting power in the case of O.P.P.A. is much greater than in the case of O.P.A. when HF is used to pre-cipitate the uranium. The amount of degradation increases with longer stirring time with HF and with longer storage time after precipitation.

4. P_2O_5 is unsatisfactory as a regenerant because an excessive amount is required. However, these solutions can be restored by addition of fresh O.P.P.A. Complete regeneration can be obtained by use of make-up O.P.P.A. in the amount of 50% to 100% of the original content.

5. Kerosene samples reclaimed from both O.P.A. and O.P.P.A. solutions appear to be identical to fresh kerosene when used as a diluent for fresh extractant.

IV. RECOVERY OF URANIUM FROM INDUSTRIAL
     PHOSPHORIC ACIDS FROM SOURCES OTHER
     THAN COMPANY A

RECOVERY OF URANIUM FROM INDUSTRIAL PHOSPHORIC
ACIDS FROM SOURCES OTHER THAN COMPANY A

Extractions of uranium from ten samples of industrial
phosphoric acids from various sources were made with butyl phos-
phoric acid solutions in benzene. The acids were first reduced
with iron. A logarithmic plot of the extraction coefficients vs.
phosphate concentration showed that the coefficient decreased
approximately as the fourth power of phosphate concentration.
This is in agreement with the data from experiments with O.P.A.
extraction of Company A acid in which phosphate concentration
was altered.

Company C Phosphoric Acid

Several extraction experiments were done with Company C
acid. The 20% P_2O_5 acid, when reduced, required only one quarter
as much O.P.A.for the same recovery as from Company A acid. When
O.P.P.A. solutions were used with unreduced 20% P_2O_5 acid, the
extraction was poorer than that from Company A acid at the same
potential. However, O.P.P.A. solutions with reduced acid gave
about the same extraction coefficients as were obtained with re-
duced Company A acid. This is in agreement with the data obtained
with Company A acid which indicated that phosphate concentration
has little effect on extraction with O.P.P.A. solutions. The
low recoveries from unreduced acid may be due to vanadium inter-
ference, oxidation state, or free fluoride content. A 1% O.P.P.A.
solution extracted 95% of the uranium from reduced acid in the
four-stage mixer-settler at room temperature using a 10:1 ratio
of acid to organic.

Uranium in Company C mixer acid (47% P_2O_5) cannot be ex-
tracted with O.P.A. solutions, since the distribution favors the
aqueous phase. O.P.P.A. solutions will extract uranium from it
but the extraction coefficients are quite low, so that about ten
times as much extractant is required as with Company A acid.

Company E Phosphoric Acid

A number of extraction experiments have been made with
phosphoric acid from Company E. This acid contains approximately
30% P_2O_5 and is similar to Company A acid. The acid, as received,
had an oxidation potential of -0.480 volts. Extraction at this
potential was poor both with O.P.A. and with O.P.P.A. solutions.
A study was made of the amount of iron necessary for reduction of
the constituents of the acid. It was found the 4 grams of highly
purified powdered iron reduced the acid to a potential of +0.200
volts. A potential of -0.240 volts was obtained with 0.3 gram
iron. The amount of iron necessary to effect a given potential is
thus about the same as that required with Company A acid.

Single-stage extractions with O.P.A. and O.P.P.A. solutions gave coefficients of about the same magnitude as those obtained with Company A acid at the same reduction potential. Extractions with O.P.P.A. at 70° C. gave coefficients about 1/3 of those at 25° C. This also is similar to the behavior of Company A acid. Treatment of Company E acid with diatomaceous earth resulted in higher coefficients with O.P.P.A.

Several runs were made in the multistage countercurrent mixer-settler using two stages and heating the acid to 70° C. Ninety-five per cent extraction of uranium was obtained with a 4% solution of O.P.P.A. in kerosene. These runs were done with a minimum of residence time of acid in the apparatus.

Company H Phosphoric Acid

Two samples of phosphoric acid have been received from Company H. One sample was an 18% P_2O_5 acid; the other was a 26% P_2O_5 acid. The 18% P_2O_5 acid contained less iron than Company A acid; the 26% acid contained slightly more than Company A acid. The 18% acid contained more fluoride than the 26% acid, but both contained less than does Company A acid.

A study was made of the amount of iron necessary for reduction. The iron used was powdered iron of high purity. It was found that 2 grams of iron per liter of acid would reduce the 18% acid to a positive e.m.f. (Pt vs. S.C.E.), but 5 grams per liter were required for the 26% acid. These results are in agreement with the original concentrations of ferric iron in the acids.

A series of single-stage extractions was made and the extraction coefficients were determined for various degrees of reduction of the acid and with various extractants. The coefficient for the extraction of unreduced 18% acid with O.P.A.-kerosene solutions was lower than that obtained with Company A acid at the same potential. As the 18% acid was reduced, however, the coefficient rose to values much higher than those with Company A acid. The unreduced 26% acid also gave low extraction coefficients, but as it was reduced the coefficient rose to about the value obtained with reduced, silica-treated Company A acid.

O.P.A. solutions containing added P_2O_5 gave higher extraction coefficients than plain O.P.A. O.P.P.A. solutions gave the highest values.

Treatment of the 18% acid with diatomaceous earth increased the coefficient obtained with O.P.A. solutions. Treatment of the 26% acid with diatomaceous earth had no effect.

The extraction was poorer at elevated temperatures in all cases, but the effect of temperature was greater with O.P.P.A. than with O.P.A.

Company K Phosphoric Acid

A sample of phosphoric acid (24% P_2O_5) was received from Company K during the period when Company K was using sulfuric acid from refinery waste streams. Thus the phosphoric acid sample was a black opaque solutions. The color was probably due to dissolved organic material. Single-stage extractions of uranium from this acid were made with amyl and butyl orthophosphoric acids. The recoveries obtained indicated that this acid is between Company A acid and Company C acid in ease of extraction.

Conclusions

The following conclusions can be drawn from the study of extraction of uranium from phosphoric acids from different sources.

1. The extraction of uranium from the acids tested does not differ significantly from the extraction of uranium from Company A acid when the phosphate concentrations of the acids are similar and the acids are reduced a comparable amount.

2. The ease of reduction is proportional to the initial concentration of iron in the acid.

3. The extraction coefficient with O.P.A. solutions varies approximately inversely as the fourth power of the phosphate concentration of the acid. There is less data with O.P.P.A. solutions, but a comparison between the coefficients obtained with Company A and Company C acids indicates that phosphate concentration has little effect when O.P.P.A. is used.

V. CONCLUSIONS AND SUGGESTIONS

CONCLUSIONS AND SUGGESTIONS

The work presented in this report has been done on a laboratory scale. The procedures and equipment are thus not entirely comparable with those which would be used in a plant. As this laboratory is located several thousand miles from the plants involved, the acid samples received here are not entirely typical of those at the plants, since they have been allowed to cool, precipitation of some constituents has probably taken place and some oxidation of the constituents may have occurred during transit. Furthermore, most of the data has been obtained with acid from one plant. While the variation in acid from plant to plant appears to be mainly a variation in phosphate content, it may be that other variables not yet appreciated will prove to alter the extraction characteristics.

It is evident then that rigid recommendations for the operation of a plant cannot be determined from this work. However, a number of suggestions can be made. The following suggestions are the result of conclusions from the work described in this report:

1. Phosphate Concentration of the Acid

If there is a choice of phosphate concentration of the acid, the lowest concentration should be chosen. In the case of O.P.A. solutions, the distribution coefficient varies inversely as the fourth power of the phosphate concentration. With O.P.P.A. solutions, the coefficient does not seem to be greatly affected by phosphate concentration. However, with lower phosphate concentrations the viscosity of the acid is less and thus the separation of the phases is easier. Density difference is also less, resulting in a slower settling rate.

2. Addition of Siliceous Materials to the Acid

There is considerable evidence that if the acid contains fluoride in excess of the amount complexed by the silica present, treatment with siliceous material will increase the distribution coefficient. The coefficient with O.P.A. solutions may be doubled or tripled by this means. The detrimental effect of fluoride is not nearly as marked with O.P.P.A.

3. Temperature of the Acid

The temperature of the acid should be as low as possible during the extraction. If O.P.A. is used as the extractant, operations at high temperatures may be feasible. However, O.P.P.A. offers so much better extraction than O.P.A. that its use is almost

imperative. O.P.P.A. loses its extracting ability at elevated temperatures because of hydrolysis or decomposition. This is a time effect, but with the lengths of time necessary for normal mixer-settler operation, it is believed that O.P.P.A. would be entirely hydrolyzed to O.P.A. in a single pass at 70° C. Thus if a mixer-settler is used for the extraction, it would probably be necessary to cool the acid before extraction. However, it may be that the extraction can be carried out at elevated temperatures if extraction apparatus with a very short holdup time, such as a Podbielniak extractor, is used.

4. Reduction of the Acid

The acid should be reduced as far as can be done cheaply without increasing the concentration of iron to a value unacceptable to the phosphate producers. If O.P.A. is used as the extractant, reduction to a positive e.m.f. (Pt vs. S.C.E.) is necessary for good recovery without excessive use of extractant. If O.P.P.A. is used as the extractant, good recovery can be obtained without reduction if the e.m.f. (for a 30% P_2O_5 acid) is -0.250 volts or greater. However, the potentials of the acids at the plants vary from these values to about -0.480 volts. In these cases some reduction is necessary. Hence, it is suggested that powdered iron be added at least in the amount of one tenth the initial concentration or that the acid be reduced to a similar extent in a column packed with scrap iron.

5. Choice of Extractant

The extraction varies with the chain length of the extractant. With ortho-phosphoric acids, there is a maximum (on a weight basis) with amyl. However, amyl ortho-phosphoric acid is somewhat soluble in aqueous solutions. The octyl derivative extracts almost as well, is cheap, and is less soluble. Hence O.P.A. was chosen for most of the work in this laboratory.

With pyro-phosphoric acids, no maximum in extraction is observed with amyl, but the extraction levels off at about octyl. Hence octyl has been used for most of the work at this laboratory. It has not been shown whether octyl or decyl is better, but octanol-2 (capryl alcohol) can be obtained cheaply and in large quantities.

O.P.P.A. offers extraction coefficients ten to one hundred times those obtained with O.P.A. However, it is hydrolyzed much more rapidly both by the phosphoric acid and by HF solutions. This disadvantage is probably outweighed by the advantage of operation with only partial reduction of the acid.

6. Preparation of the Extractant

O.P.P.A. solutions have been found to deteriorate rather rapidly with time at room temperature. Samples kept under refrigeration seem to be quite stable over periods of several weeks, but it would probably be simpler and cheaper to prepare the extractant daily at the plant rather than to prepare it elsewhere and ship and store it under refrigeration.

The method of preparation which has been found to yield the extractant with the greatest extracting power consists of the following steps:

      a. Slurry P_2O_5 in kerosene. The optimum ratio is about 0.1 gram P_2O_5 per ml. of kerosene.

      b. Add the alcohol to the slurry, with stirring, and, preferably with cooling, in the ratio of 2 moles of alcohol to 1.0 moles of P_2O_5.

7. Diluent

The extractants are diluted with a solvent before use. It is believed that kerosene is the best diluent to use as it is cheap and gives distribution coefficients about as high as those with any solvent tried. The kerosenes used were commercial products from western crudes. Highly purified kerosene resulted in poorer extractions. Diesel oil is cheaper but some types result in lower distribution coefficients.

8. Methods of Contacting

It is believed that countercurrent-multistage operation is necessary for efficient extraction. An economic balance is needed between the variables of reduction, temperature, and number of stages. From the data available, three to four stages seem to be the economic maximum. It is possible that a Podbielniak extractor will prove superior to mixer-settlers for extraction of acid at elevated temperatures because of the short holdup time in this apparatus.

9. Recovery of Uranium from the Extract

The simplest method of recovery of uranium is by precipitation with HF. Nearly quantitative precipitation from either O.P.A. or O.P.P.A. can be obtained by adding about one pound HF per pound of U_3O_8. Cake grades run over 50% U_3O_8. Addition of HF as 48% to 60% solutions has proven satisfactory. Dilute HF solutions cause emulsion formation; anhydrous HF causes excessive deterioration of the extractant.

All precipitations at this laboratory have been done at room temperature. At higher temperatures it is possible that hydrolysis of the extractant may be accelerated. Thus, if it is found possible to extract at elevated temperatures, it may be necessary to cool the extractant before precipitation.

It is believed that contact with HF accelerates the hydrolysis of the extractant. Thus the residence time during precipitation, filtration, and holding before recycle should be as short as possible to keep the amount of degradation of the extractant to a minimum.

10. Recycle of Extractant

It is economically advantageous to recycle the extractants. Due to solubility, hydrolysis, and degradation of the extractant during the extraction and precipitation, it is necessary to use regenerative treatment between cycles to restore the extractant to its initial efficacy. It has been found that O.P.A. solutions can be so restored by addition, with agitation, of 0.1 pound P_2O_5 per pound of contained O.P.A. O.P.P.A. solutions can be restored by addition of fresh O.P.P.A. in the amount of 50% to 100% of the original concentration. There is no indication that the kerosene diluent is altered in the process, so it is believed that it can be re-used indefinitely.

11. Pilot Plant

It is recommended that one comprehensive pilot-plant study be completed prior to application to a full-scale plant. The laboratory work presented in this report indicates a number of alternative procedures which must be studied on a larger scale before definite conclusions can be drawn as to the optimum operating conditions. The same recovery may be obtained with a low distribution coefficient as with a high coefficient if the number of stages is increased and if the ratio of extractant to acid is increased. Hence economic balances must be made between the following factors:

        a. Reduction of acid vs. number of stages.
        b. Addition of silica vs. number of stages.
        c. Cooling of acid vs. number of stages.
        d. Combination of a, b, and c vs. number of stages.
        e. Cooling of acid vs. possible greater amount of make-up of extractant.
        f. Number of stages vs. flow-rate ratio of acid to organic.
        g. Optimum degree of mixing and corresponding settling times required.

Larger scale work is also needed to determine the losses and material balances that would be encountered in a commercial plant.

VI. <u>APPENDIX</u>

APPENDIX

A. Analytical Methods

Analysis of Uranium

Fluorimetric

Phosphoric acid solutions were analyzed for uranium by the procedure described in DOW-65. The organic solutions were analyzed for uranium by a variation of the same method. Aliquots of the samples were evaporated to dryness. Concentrated HNO_3, containing a little concentrated H_2SO_4, was added and the solution was boiled to SO_3 fumes to decompose the organic. $HClO_4$ was then added dropwise to remove any traces of carbon that remained. The solution was diluted to a known volume and an aliquot was taken and analyzed by the fluorimetric procedure.

Colorimetric

The organic extracts can also be analyzed for uranium (IV) by a colorimetric method. The absorption spectum of uranium (VI) shows peaks only in the region where O.P.A. and O.P.P.A. adsorb strongly. Hence no attempt has been made to develop a colorimetric method for the determination of uranium (VI). The absorption spectra of uranium (IV), however, shows seven maxima in the region from 400 to 1200 mμ.

Figure 5 shows the absorption spectra of uranium (IV) in a 10% solution of O.P.A. in kerosene. Pure kerosene was used as a reference. Below 600 mμ there is appreciable adsorption of light by the organic constituents. The absorption curves for uranium (IV) in O.P.A., O.P.P.A., and concentrated H_3PO_5 are almost identical. The uranium peaks at 630, 665$\frac{1}{2}$, and 1130 mμ have been studied with synthetic solutions of uranium (IV) in 10% O.P.A.-kerosene. The maximum at 665 mμ has the greatest molar extinction coefficient.

The optical densities of solutions of known uranium concentration were measured at these points. A study was made of the interference of various metals and it was found that the effects could be minimized if the differences in optical density between selected maxima and minima were used. Curves of these differences vs. concentration were used as calibration curves.

Similar curves were obtained for 1%, 2%, and 10% O.P.P.A. solutions in kerosene. The method has been found to be quite selective for uranium.

Figure 5. Absorption Spectra of U(IV) in 10% O.P.A.
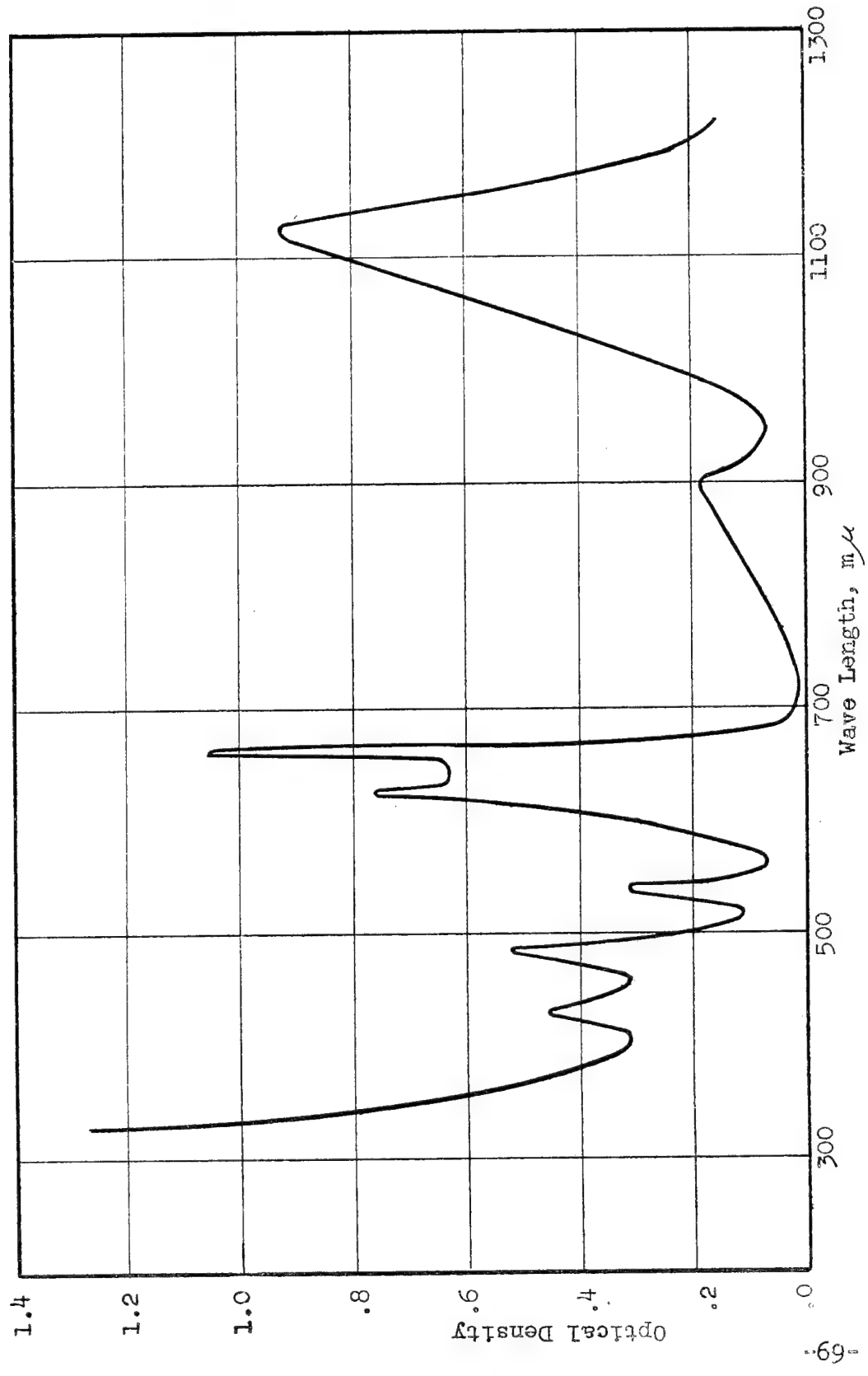
Analysis of Alkyl Phosphates

Ortho-phosphates

Alkyl ortho-phosphates were analyzed for the amount of mono- and di- compound by titrating in an acetone water solution with 0.1 N NaOH. The titrations were followed with a Beckman pH meter.

Pure mono-O.P.A. has two breaks in the titration curve: one at pH 9, indicating a weak acid; and one at pH 4 or 5, indicating an equal amount of strong acid. Pure di-O.P.A. has only one break in the titration curve, at pH 4 or 5, indicating a strong acid. The relative amounts of mono- and di- O.P.A. in a given mixture can thus be determined from the amounts of strong and weak acid indicated by the position of the breaks in the titration curve. The sharpest curves were obtained by using 40% acetone in the solution. Infrared adsorption was used to determine the concentration of O.P.A. in CCl4 solutions. However, this method could not be used to distinguish between mono- and di-O.P.A. as the adsorption curves of these components were almost identical.

Pyro-phosphates

A method of estimation of the composition of alkyl pyrophosphate mixtures was developed on the assumption that the pyro- and meta-phosphates in the mixture can be completely hydrolyzed without hydrolyzing the ortho-phosphates. From the titration curves and the ortho-phosphoric acid determination of unhydrolyzed and hydrolyzed samples, sufficient data is obtained to set-up six equations with ten unknowns. Obviously the equations cannot be solved completely to determine the composition of each component, but limits of the magnitude of groups of components can be determined. By making assumptions as to the concentration of some of the members in these groups, self-consistent estimates of the composition of the mixtures can be obtained.

This method assumes that no hydrolysis occurs during the first titration and that full hydrolysis of the pyro-'s occurs during the HCl treatment.

B. **Symbols Used in this Report and in the Monthly Progress Reports**

C_O - The uranium concentration in the organic phase.

C_O^* - The uranium concentration in the undiluted extractant.

C_{max}^* - The limiting uranium concentration in the undiluted extractant as $C_A \rightarrow \infty$.

C_A - The uranium concentration in the aqueous phase.

C_H - The uranium concentration in the head acid.

V_O - The volume of the organic phase.

V_A - The volume of the aqueous phase.

K_D - The extraction coefficient = C_O/C_A.

$K^{\star}$ - The coefficient of the extraction into undiluted extractant = $\dfrac{C_O^{\star}}{C_A}$.

K - Was used in a few early reports to indicate either K_D or $K^{\star}$.

$K_{max}^{\star}$ - The limiting value of $K^{\star}$ as $C_A \rightarrow 0$.

B.P.A. - Butyl ortho-phosphoric acid.

A.P.A. - Amyl ortho-phosphoric acid.

O.P.A. - Octyl ortho-phosphoric acid.

O.P.P.A. - Octyl pyro-phosphoric acid.

e.m.f. - Oxidation potential, Pt vs. S.C.E.

The sign convention used is: higher oxidation = more negative.

PART II. INDEX OF TOPICS IN MONTHLY PROGRESS
         REPORTS CONCERNING THE RECOVERY OF
         URANIUM FROM INDUSTRIAL PHOSPHORIC
         ACIDS BY SOLVENT EXTRACTION

INDEX OF TOPICS IN MONTHLY PROGRESS REPORTS
CONCERNING THE RECOVERY OF URANIUM FROM
INDUSTRIAL PHOSPHORIC ACIDS BY SOLVENT EXTRACTION

This index has been compiled as an aid in obtaining data from the Dow monthly progress reports. The period covered is from March, 1951, through June, 1952. The index also includes references to Part I of this report. As in any body of research covering a long period of time, there are no doubt some erroneous results, misinterpretations and contradictions. In this study, much of the earlier work was exploratory and hence, of a less quantitative nature than the later work. It is believed that, in general, where there is a disagreement in the data, the latest data should be considered the more precise.

The topics are presented in the same order used in Part I of this report. In Part I, however, the work with synthetic acids was included in the work with Company A acid as the experiments with synthetic acids were done for comparison. In the index the synthetic acid experiments are listed in a separate heading under "Extraction from Acids Other Than Company A." The following are the principal topics covered.

I. Extraction of Uranium from Company A Phosphoric Acid

 A. Measurement of Magnitude of Extraction
 B. Study of Variations in the Acid
 C. Study of Extractants
 D. Multistage Countercurrent Extraction
 E. Recovery of Uranium from the Extractants
 F. Recycle and Restoration of the Extractants

II. Extraction from Acids Other Than Company A

III. Analytical Methods

The references are indicated by the number of the progress report, which is underlined, followed by the page number. Thus 56 45 indicates page 45 of Dow-56 (progress report for June, 1951). Where the reference is to several pages which follow one another, the first page only is indicated.

I. Extraction of Uranium from Company A Phosphoric Acid

    A. Measurement of Magnitude of Extraction

    B. Study of Variations in the Acid

I. Extraction of Uranium from Company A Phosphoric Acid

I. **Extraction of Uranium from Company A Phosphoric Acid**

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